Institute of Paper Science and Technology

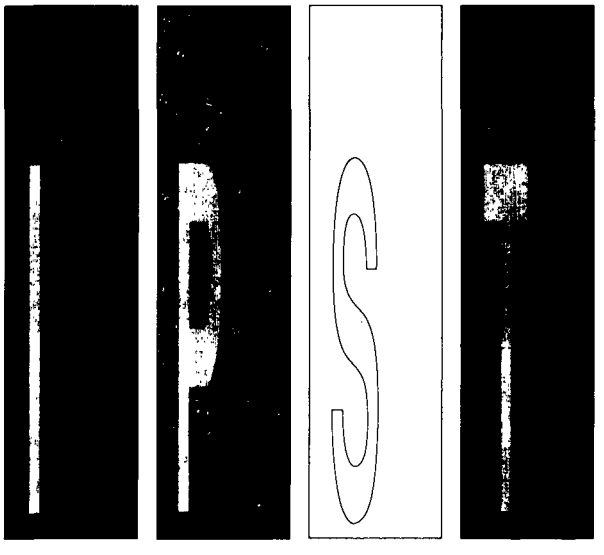
STATUS REPORTS

To The

CHEMICAL PULPING AND BLEACHING

PROJECT ADVISORY COMMITTEE

April 28, 1993



Atlanta, Georgia

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
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The Institute of Paper Science and Technology is a unique organization whose charitable, educational, and scientific purpose evolves from the singular relationship between the Institute and the pulp and paper industry which has existed since 1929. The purpose of the Institute is fulfilled through three missions, which are:

- to provide high quality students with a multidisciplinary graduate educational experience which is of the highest standard of excellence recognized by the national academic community and which enables them to perform to their maximum potential in a society with a technological base; and
- to sustain an international position of leadership in dynamic scientific research which is participated in by both students and faculty and which is focused on areas of significance to the pulp and paper industry; and
- to contribute to the economic and technical well-being of the nation through innovative educational, informational, and technical services.

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CHEMICAL PULPING AND BLEACHING

ANNUAL RESEARCH REVIEW

APRIL 28, 1993

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
500 10TH STREET, N.W.
ATLANTA, GEORGIA 30318

CHEMICAL PULPING AND BLEACHING
ANNUAL RESEARCH REVIEW
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SULFUR-FREE SELECTIVE PULPING PROCESS

PROJECT 3661

Donald R. Dimmel
Xiaoqi Pan
and
the staff at National Renewable Energy Laboratory
(Golden, CO)

ANNUAL RESEARCH REVIEW
APRIL 28, 1993

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
500 10TH STREET, N.W.
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TECHNICAL PROGRAM REVIEW FORM

PROJECT TITLE: SULFUR-FREE SELECTIVE PULPING PROCESS

PROJECT STAFF: Donald R. Dimmel and Xiaoqi Pan, and staff at the National Renewable Energy Laboratory (Golden, CO)

BUDGET (FY 93-94): Projected $150,000

REPORTING PERIOD: March 1992 - February 1993

DIVISION: Chemical and Biological Sciences

PROJECT NUMBER: 3661

OBJECTIVE: The objective of this project is to develop the synthesis of a low-cost catalyst which, when used in pulping systems, will increase pulping rates and product yields, while reducing the dependence on sulfur additives. The process under investigation is based on conversion of an inexpensive pulping by-product, lignin, to a useful quinone-type pulping catalyst.

IPST GOAL: Improved pulping processes

SUMMARY:

A joint research effort between the Institute of Paper Science and Technology and the National Renewable Energy Laboratory is being conducted on ways to produce cost-effective pulping catalysts from lignin. The principal focus of the research has been to optimize the yields of catalyst synthesis from a low-molecular-weight lignin. The process involves treating the lignin with an inexpensive oxidizing agent to give a mixture of methoxy-substituted benzoquinones and then converting the benzoquinones into anthraquinone pre-

cursors by treatment with a diene, using the well-known Diels-Alder reaction. The most important factor in the cost of anthraquinone catalysts prepared from lignin is the overall yield of the chemical processing steps.

A combination of improvements in the isolation, oxidation, and Diels-Alder steps has resulted in a six-fold increase in overall yield and a concomitant reduction of the projected anthraquinone amortized production cost by over a factor of ten since the beginning of the research program to a cost below the current selling price of AQ. However, further improvements are needed to reach our targeted price of $1.00-1.50/lb.

Recent research activity at IPST has addressed the issue of whether NO_2/O_2 can oxidize internal lignin units in the polymer and not just phenolic end units. Based on studies with lignin model dimers, we now have evidence that non-phenolic (internal-type lignin units) are not converted to benzoquinones under present oxidation conditions. The dimer models will be used to explore alternative conditions which may lead to greater oxidation.

Other research activities within the last year have included: (1) characterization of copper oxide treated lignin by thioacidolysis techniques; (2) improvements in benzoquinone yields from guaiacyl-type lignin units by brominating prior to NO_2/O_2 oxidation; and (3) examination of effective ways to isolate benzoquinone products from NO_2 oxidation liquors.

Future research will focus on evaluating different starting materials, improving the yields of the synthetic steps, optimizing process steps, and evaluating the properties and performance of pulps which result when using the new catalysts, both in the absence of and in combination with sulfur additives.

The scale of the lignin-to-catalyst process will be progressively increased in size, thus, allowing more complete evaluation of the process steps and product characteristics. The size will be sufficient for updating technoeconomic assessments and for demonstrating the feasibility of each stage of the process prior to pilot plant operation and transfer of the technology to the industry.

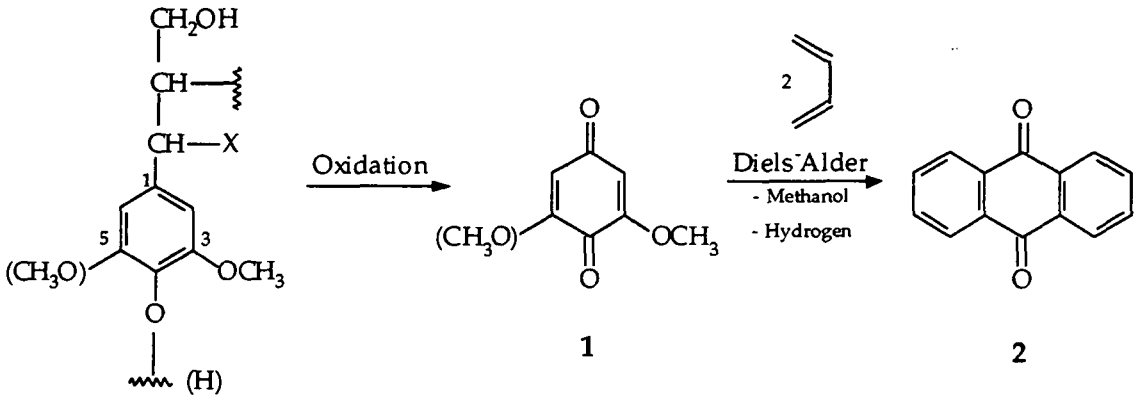
BACKGROUND AND REVIEW OF PAST PROJECT ACTIVITY

A process is under development at IPST and NREL to improve selectivities and reduce the levels of sulfur chemicals used in pulping. Improved selectivity means increases in pulping rate and yields, which translates to greater mill productivity, conservation of wood, and less energy required per ton of product. Less sulfur means a simplified chemical recovery process, lower odor emissions, and a decrease requirement for bleaching chemicals, meaning less organics being discharged to rivers.

The project is focused on synthesizing a low-cost anthraquinone (AQ) catalysts from lignin. The research at NREL compliments IPST research by examining alternative chemical synthesis methods, by providing ways to get suitable lignin starting materials, and by conducting technoeconomic evaluations. A very detailed description of the project and the research results to date is available in our publications[1-6] and in the annual reports to DOE.[7-11] The discussion which follows summarizes project work through October 1992, excluding early dimer synthesis efforts; the latter is the subject of discussion in the next section, which principally covers work from November 1992 and end of February 1993.

A low-molecular-weight lignin is treated with an inexpensive oxidizing agent to give a mixture of methoxy-substituted benzoquinones (Fig. 1, structure **1**), which are converted into nonaromatic anthraquinone precursors by treatment with a diene (Diels-Alder reaction). Final conversion of these precursors to AQ derivatives occurs by loss of methanol and hydrogen, either during reaction or in a separate step (Fig. 1). The aromatization step may be unnecessary; partially aromatic anthraquinone also functions as a pulping catalyst by <u>in situ</u> conversion to AQ.

Technoeconomic Evaluation. Our most recent evaluation,[9] based on actual laboratory conditions and yields, continues to support the contention that a lignin-to-AQ process is an attractive economic approach, that AQ from organosolv lignin would be ~25% cheaper than one based on kraft lignin, and that the single most important determining factor in the final cost of AQ catalysts from lignin is the overall yield of the chemical processing steps.



Lignin DMBQ = two OCH_3 groups MMBQ = one OCH_3 group Anthraquinone

Figure 1. Chemical steps in the conversion of lignin to an AQ.

Lignin Processing. Three lignin sources and two extraction techniques have been the focus of our early investigations. The three lignins are kraft lignin (from black liquor acidification), precipitated organosolv lignin, and soluble organosolv lignin. Kraft lignin is an attractive raw material for this project because of its wide availability. However, the conditions of the kraft process significantly alter the native lignin structure, removing a portion of the functional groups important for further chemical processing. Kraft lignin also contains a fairly large percentage of high-molecular-weight material.

Organosolv lignin is the lignin which precipitates during evaporation of the pulping liquor from a pulping process that employs an organic solvent. Organosolv lignin retains certain native functional groups that make subsequent chemical processing easier. It also contains a high proportion of the low-molecular-weight lignin and is relatively inexpensive. Complete evaporation of the solvent from an organosolv pulping process provides a residue which contains very low-molecular-weight lignin. This "soluble" lignin should be an ideal starting material for catalyst synthesis; however, the lignin is contaminated by other liquor components and only limited studies have been performed on this material. A potential drawback to the use of organosolv lignins is the current limited number of commercial sources.

The isolation of low-molecular-weight lignin from kraft and other lignin

sources by supercritical fluid extraction has proven to be quite effective; however, the isolated yields were low.[12] Encouraging results have been obtained by the simple extraction of organosolv lignins with organic solvents; here we recovered a relatively high yield of low-molecular-weight lignin which responded well to subsequent chemical transformations.

Oxidation Studies. Many lignin models have been oxidized to benzoquinones (**1**, Fig. 1) in about 90% yields with hydrogen peroxide (alone or with metal catalysts). Syringyl models (lignin units with two methoxyl groups per ring) have also been oxidized in high yield with oxygen in the presence of metal catalysts or nitrogen dioxide. In contrast, the oxidation of guaiacyl models (lignin units with one methoxyl group per ring) with O_2/metal or NO_2/O_2 gave poor yields of monomethoxybenzoquinone (MMBQ). In actual lignin oxidation studies, we have observed 15% yields of dimethoxybenzoquinone (DMBQ) from NO_2/O_2 oxidation of a low-molecular-weight hardwood lignin; this yield represents reaction of about 60% of the available syringyl units to DMBQ. Less than 1% MMBQ was observed in these cases. Peroxide oxidations of lignin samples did not appear to give any better yields of benzoquinones, although the relative amount of MMBQ was more.

The NO_2 oxidation of lignin is usually carried out in methanol; as the reaction proceeds, DMBQ precipitates. The solubility of DMBQ in methanol was measured to be 0.45 g/l. Simple filtration of a mixture of DMBQ in methanol should provide a large portion of the available DMBQ. Steam distillation proved ineffective as a way to recover DMBQ from a water mixture. Precipitated lignin residues absorbed some DMBQ, leading to a lower recovery yield. This should not be a problem with methanol-soluble low-molecular-weight lignin. We have shown that 95% of DMBQ was recovered from a mixture of DMBQ and copper oxide treated lignin in methanol. Consequently, filtration appears to be a convenient and efficient manner to isolate DMBQ from NO_2 oxidation mixtures; it may be less effective with other benzoquinones.

The low yields of MMBQ with NO_2/O_2 oxidation limit the amount of useful benzoquinones that can be generated from most wood species, since guaiacyl lignin units are the dominant units in softwoods and a significant unit in

hardwoods. Model experiments have suggested a preference for addition of NO_2 to the 5-position of guaiacyl structures over oxidation to a benzoquinone. Model compounds which contain a blocked 5-position, such as 5-bromovanillin, provided a 55% yield of DMBQ from NO_2/O_2 oxidation. Thus, improved benzoquinone yields from guaiacyl units are possible by structural modifications; however, such an approach may be costly.

Degradation of lignin into smaller fragments before performing NO_2/O_2 oxidation has resulted in higher yields of benzoquinones. The best lignin pretreatment was copper oxide oxidation, where the DMBQ yield was six times greater than that of a non-pretreated sample in some cases. The yield of benzoquinone correlated reasonably well with the concentration of syringaldehyde in the lignin sample. Thioacidolysis studies have shown that the copper oxide treatment effectively destroyed the β-O-4 linkages of the lignin and gave mostly syringyl-type monomeric products, such as syringaldehyde.

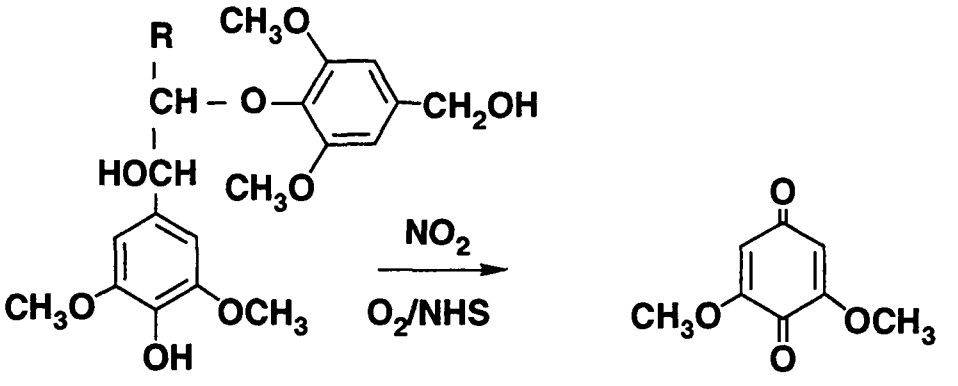
There appears to be two ways to get high (on a relative basis) yields of DMBQ from NO_2 oxidation of a lignin. One is to lower the molecular weight of a whole lignin with treatments, such as copper oxide, before performing the NO_2/O_2 oxidation. The other is to extract a lignin sample to obtain a low-molecular-weight fraction before NO_2/O_2 oxidation.

Diels-Alder Studies. This step is designed to add two rings simultaneously to the starting benzoquinone by reaction with dienes. Developmental research has shown that good conversions of benzoquinones to AQ or AQ-like structures can be achieved using water as a solvent, isoprene as the diene, and DMBQ as the benzoquinone. Catalysts in organic solvents have also proven useful in getting two rings to form simultaneously. The selection of the solvent depended on the type of benzoquinone employed.

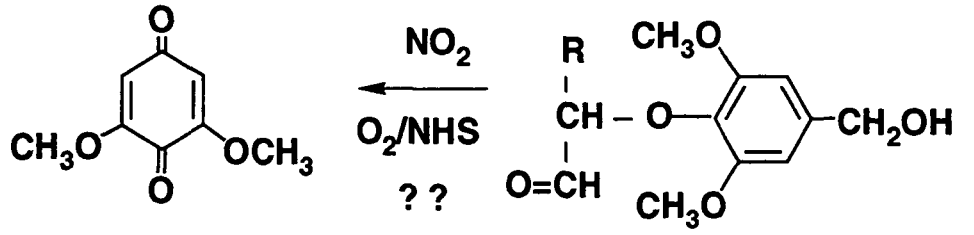
Pulping Studies. Several Diels-Alder reactions have been performed in water to obtain small quantities of naphthaquinone/AQ product mixtures. However, each of the samples has encountered difficulties in either product purification or in pulping activity testing; conclusive test results for the catalyst mixtures are not yet available. The most abundant component of the mixture, dimethyl-AQ, has been shown to be a superior pulping catalyst.

RECENT RESEARCH RESULTS

One of the big questions which surrounds our research is whether or not an oxidizing agent, such as NO_2/O_2 or H_2O_2/metal, can progressively oxidize lignin units which are internal units in the polymer and not phenolic. In other words, if the first phenolic unit is oxidized to a benzoquinone, will the the side chain of the first unit be lost, producing another phenol for reaction? If the answer is "no," then it is important that we use very small lignin fragments as starting materials in the catalyst synthesis. Oxidation of lignin model dimers **3** and **4**, shown below, will help establish this point; production of two benzoquinones per dimer model upon oxidation would prove that the side chain breaks down to allow both the phenolic and nonphenolic aromatic rings to be oxidized. We are assuming that structures **5** and **6** would be formed in the initial oxidation; the question is whether such structures (produced from a model or from lignin) would oxidize further.



3, R = H
4, R = CH_2OH



5, R = H
6, R = CH_2OH

We attempted a synthesis of the β-O-4 dimer **3**, using the synthetic route shown in Figure 1, which consisted of: (1) bromination of acetosyringone, (2) preparation of sodium 4-formyl-2,6-dimethoxyphenonate, (3) coupling the products of steps 1 and 2 to get β-(4'-formyl-2',6'-dimethoxyphenoxy)acetosyringone, and (4) $NaBH_4$ reduction of the latter compound. Various attempts to obtain a pure product were not successful.

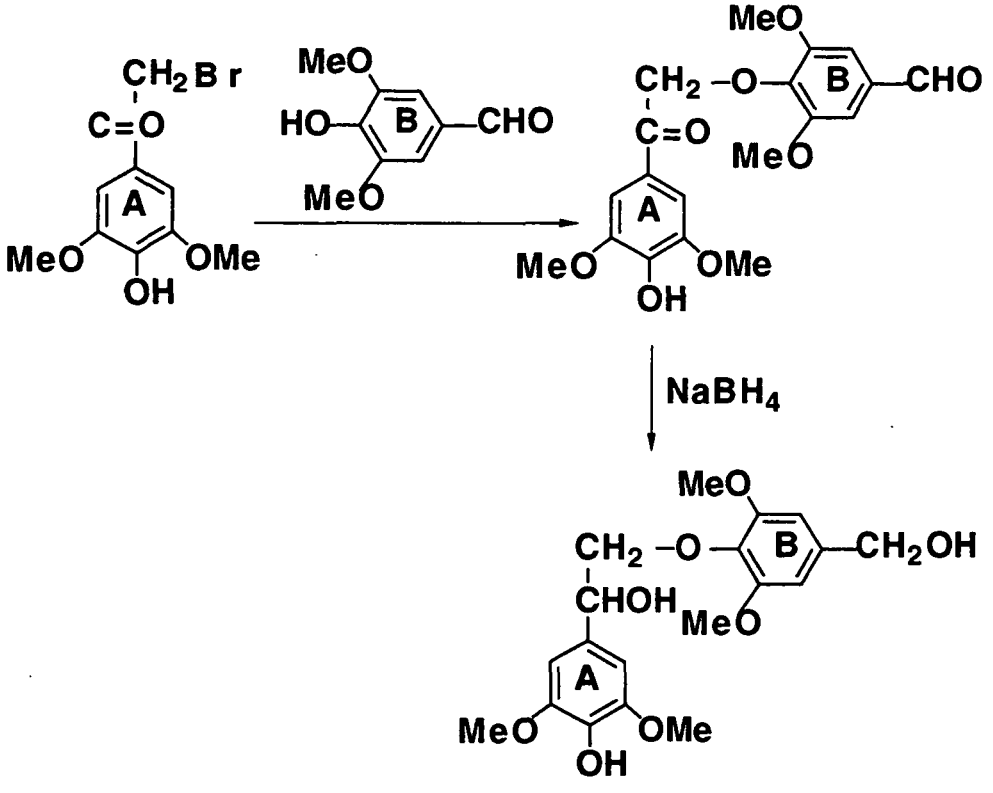
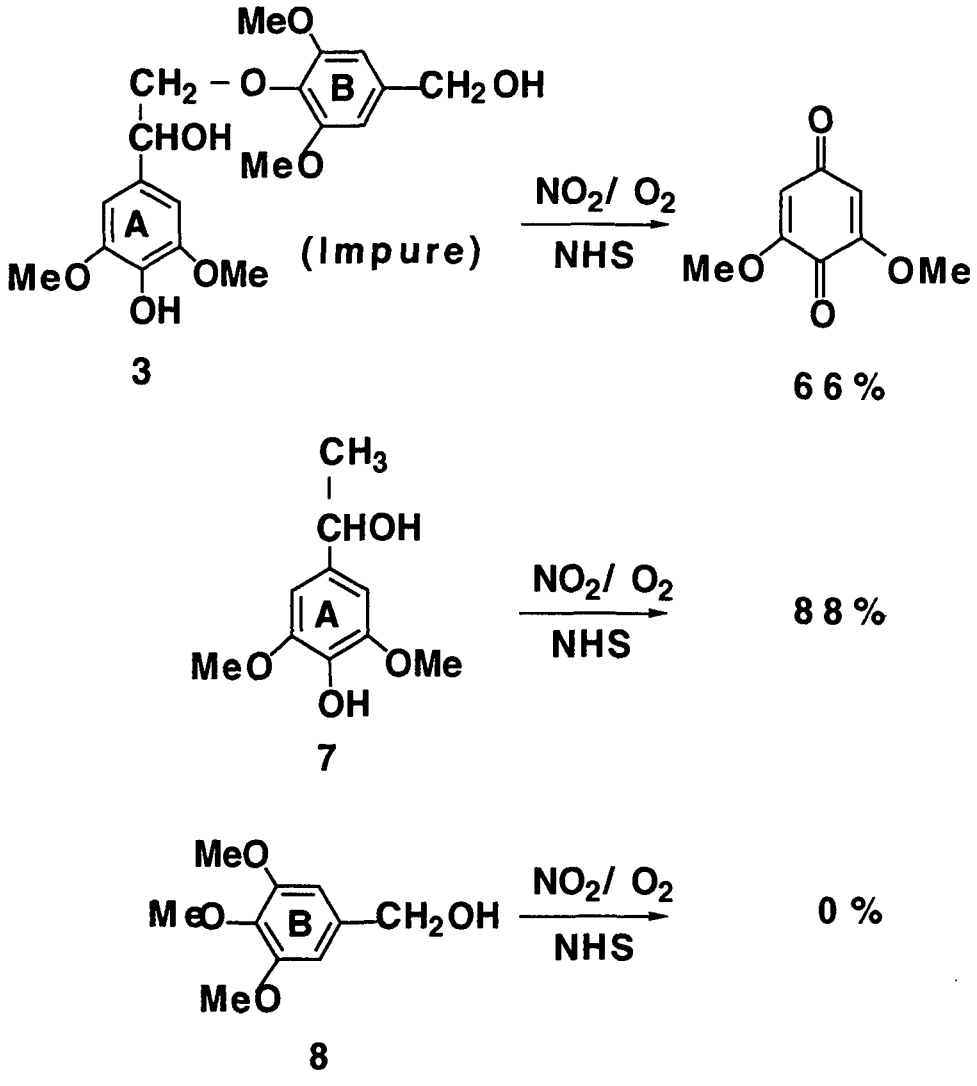


Figure 1. Synthesis of the β-O-4 dimer **3**.

The crude model dimer **3** (estimated by NMR to be approximately 90% pure) was oxidized with NO_2 to give a 66% yield of DMBQ. The oxidation yield indicated that only one of the two rings, presumably ring A, had oxidized.

Several model compounds were submitted to NO_2 oxidation to determine effects of substrate structure on the yield of DMBQ. Acetosyringone gave a 31% yield of DMBQ. Its reduced counterpart, α-methylsyringyl alcohol (**7**), gave a 88% yield of DMBQ; a non-phenolic model compound, 3,4,5-trimethoxybenzyl alcohol (**8**), provided no DMBQ (Fig. 2). The yield with α-methylsyringyl alcohol is comparable to that of syringyl alcohol. It is known that syringaldehyde and syringyl alcohol oxidize in similar yield (~90%) to

DMBQ. Interestingly, α-methyl substitution has little effect for the alcohol, but considerably reduces the yield of DMBQ from a carbonyl side chain.



3 7 8

Figure 2. Oxidation of selected lignin models.

Analysis by GC and by GC-MS of the NO_2 reaction solution from the non-phenolic model **8** showed starting material (60%) and a signal (40%) which contained two components: 3,4,5-trimethoxybenzaldehyde (**9**) and 3,4,5-trimethoxybenzyl methyl ether (**10**) (Fig. 3). The latter probably came from an acid catalyzed reaction of the benzyl alcohol with methanol solvent; the former came from oxidation of the benzyl alcohol. The results indicate that the presence of free phenolic hydroxyl groups in the substrate is essential to conversion to DMBQ and that the NO_2/O_2 conditions result in some benzyl alcohol oxidation to an aldehyde.

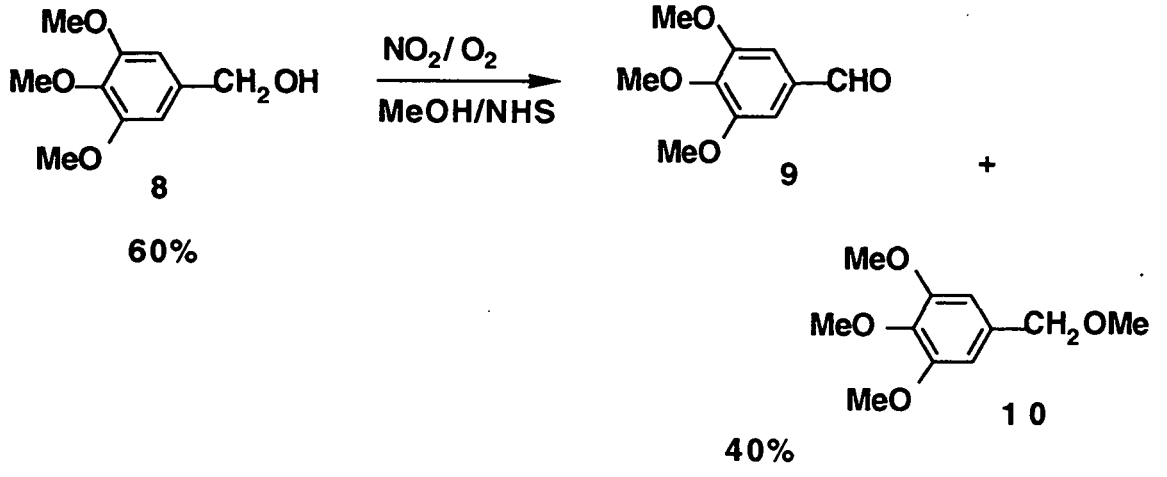


Figure 3. Oxidation of lignin model compound 8.

If we consider that the β-O-4 dimer (**3**) is composed of a "combination" of α-methylsyringyl alcohol (**7**) and 3,4,5-trimethoxybenzyl alcohol (**8**), the ceiling yield of DMBQ from the dimer should be about 80%. We observed a 66% yield of DMBQ from oxidation of the crude dimer with NO_2. We tentatively conclude that only the syringyl units located at terminal positions of a lignin macromolecule will give DMBQ. This significant, but tenuous conclusion needed verification with a pure dimer. Unfortunately, as will be discussed below, we encountered a number of problems in getting a pure dimer.

In our second attempt at a syringyl-syringyl dimer, we sought a more representative type of dimer, one with a three carbon side chain, and enough flexibility to give a choice of an alcohol or aldehyde group on the B ring. Models with three carbon side chains have erythro and threo stereoisomers; to simplify isomer separation, we attempted a synthesis based on the use of a sterically hindered ester, which we expected would only lead to one stereoisomer. The projected synthesis of dimer **4** by this route is outlined in Fig. 4.

The initial synthesis of the syringylglycerol-β-syringyl alcohol ether (**4**) involved: 1) benzylation of syringaldehyde to give **11**; (2) preparation of syringyl acetal using ethylene glycol; (3) preparation of 2,6-diisopropylphenyl bromoacetate by coupling 2,6-diisopropylphenol and bromoacetyl bromide; (4) coupling the products of steps 2 and 3 to get 2,6-diisopropylphenyl (4-ethylene acetal-2,6-dimethoxyphenoxy) acetate (**12**); (5) condensation of the products of

steps 1 and 4 to get the β-hydroxy ester derivative (**13**); (6) $LiAlH_4$ reduction of compound **13** to yield a 1,3-diol derivative (**14**); (7) catalytic hydrogenation of compound **14** to remove the benzyl group; (8) acidic hydrolysis of compound **15** to remove the acetal group; and (9) $NaBH_4$ reduction of compound **16**.

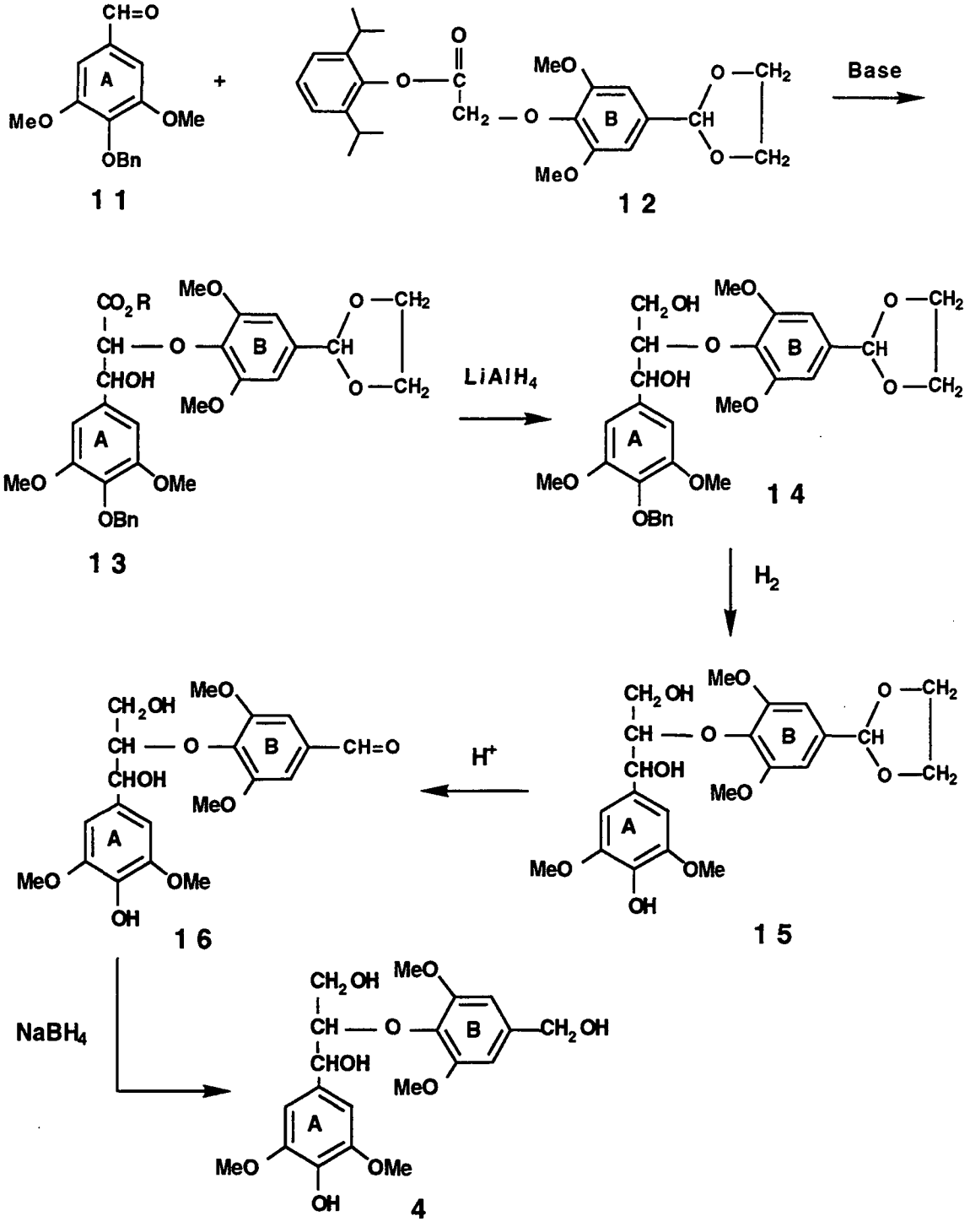


Figure 4. First attempted synthesis of lignin model compound 4.

The key step in the synthetic route was condensation of benzyl syringaldehyde (**11**) with the hindered ester (**12**) in the presence of lithium diisopropylamine (LDA). The condensation was performed twice and, in each case, produced a complex mixture. Chromatography of the products showed that the reaction was incomplete; partial hydrolysis of the acetal on ring B also apparently occurred during the chromatography, making the reaction mixture even more complex. Considerable time was exhausted in attempting to purify the product; however, the oil resisted crystallize from various solvent combinations, the expected compound (**13**) was too large to distill, and silica gel chromatography, without decomposition, was not possible. The product mixture was submitted to the remaining synthetic steps, without successful purification of any of the intermediate compounds. The final product was a complex mixture of components which could not be purified to provide model **4**.

A modified synthetic route was initiated using a less hindered ester in the condensation step. The bulky 2,6-diisopropyl-phenyl group, which was selected to control the stereochemistry during the condensation, might have been too crowded and hampered the reaction. Dr. G. Brunow has been successful in preparing a β-O-4 dimer containing two syringyl units by employing a much less hindered enolate. Our second attempt at the synthesis of dimer **4** involved a condensation of benzyl syringaldehyde (**11**) with ethyl 4-diethylacetal-2,6-dimethoxyphenoxyacetate (**17**), as outlined in Fig. 4.

Compound **17** was prepared by coupling syringaldehyde and ethyl chloroacetate, followed by treatment with triethyl orthoformate and *p*-toluenesulfonic acid. Much time was spent attempting to purify this compound. However, it was found to be unstable, even towards crystallization from ethanol. This suggests that the compound **17** should be used quickly after preparation; further purification was not attempted. Fortunately, the acetal derivative **17** could be obtained in a high yield; only minor quantities of impurities were seen by thin layer chromatography (TLC).

The condensation of **11** and **17** proceeded well; TLC of the products showed one major component, without any significant amount of remaining starting

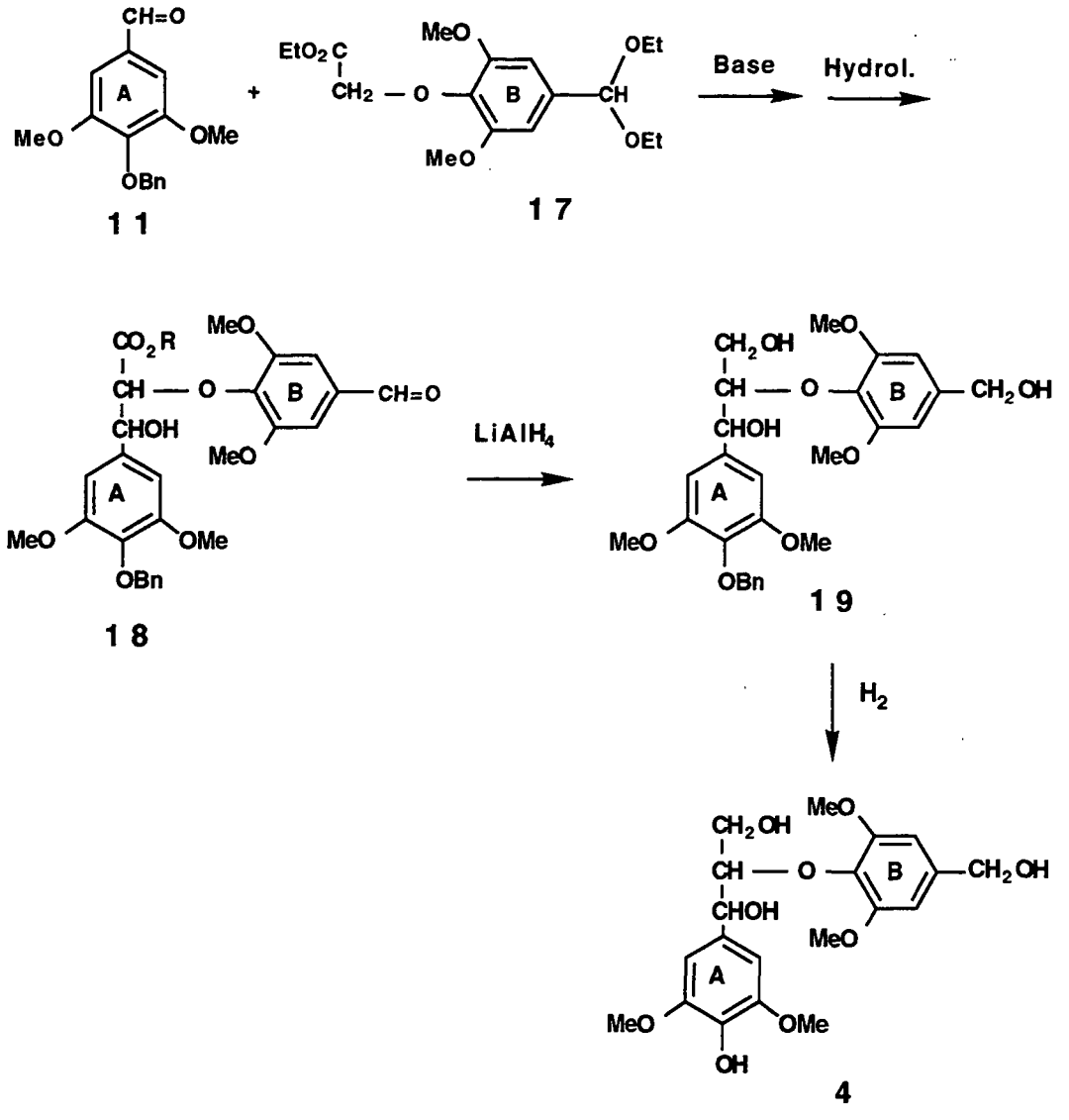


Figure 4. Second attempted synthesis of lignin model compound 4.

materials. The major component was most likely an erythro/threo mixture of β-aryl ether acetals. The acetal components were converted into their more stable aldehyde counterparts (**erythro/threo 18**) by acidic hydrolysis and subjected to chromatography on silica gel. The mixture was partially separated by column chromatography. The minor threo isomer was easily recrystallized; the major erythro isomer was about 95% pure; further purification attempts were not successful. Good spectral data wre obtained for both isomers.

Each isomer was taken through the next synthetic steps to generate **erythro 4**

and **threo 4**. A recrystallized sample of **threo 4**, having a sharp melting point (equal to a literature value), was obtained. The erythro isomer again resisted recrystallization attempts; the material is a solid with a broad melting point range. Based on NMR analysis, we concluded that both compounds were pure; however, NMR is only accurate to about ±5%, which means that **erythro 4** is ≥95% pure.

Both **erythro 4** and **threo 4** were subjected to duplicate 2-hour NO_2/O_2 oxidation reactions. The former gave DMBQ yields of 75 and 76%, the latter gave 88 and 91% yields. The yield differences for erythro and threo were probably due more to stereochemical differences than to purity differences. Interestingly, we also observed two coproducts corresponding to the anticipated C_α-C_β cleavage. These components were tentatively identified as **6** and an oxidation (α-aldehyde) analog of **6**; verification of the structures is now in progress.

The results of the lignin dimer oxidation studies clearly indicate that the phenolic (A) ring is oxidized to DMBQ, but that the nonphenolic piece, which is cogenerated, does not break down to a phenol and further oxidize to DMBQ. These dimer oxidation studies will be continued. Conditions will be sought which will break the linkage between ring B and the side chain of attached unit in the presence of NO_2/O_2 to activate oxidation of non-phenolic (lignin) units.

FUTURE ACTIVITY

The objective of future research will be to move the successful results of the laboratory research to a larger scale. Our primary focus will be to prepare the best possible package to present to the industry for technology transfer. However, the scale up effort needs to be supported by continued research in process improvement to assure that a most cost-effective approach is taken. Each component of the process will be subjected to a technoeconomic evaluation and judged for its overall merit.

Lignin Processing. Regardless of the lignin source, scale up of the extraction is an important step in development of a commercial process. A number of different features must be considered since each has a bearing on the overall economic feasibility of the process. These features include:

- assessment of appropriate sources of lignin, i.e., extraction of an isolated lignin or crude pulping liquors,
- comparison of the yield of low-molecular-weight material obtained on a larger scale process to that of the laboratory scale,
- the physical characteristics of a given low-molecular-weight lignin, such as detailed structure, average molecular weight, etc., both before extraction and after isolation of the low-molecular-weight material,
- the performance of the low-molecular-weight lignin in subsequent chemical processing, and
- the economic feasibility of the proposed extraction, based on the material balance of the extraction process and the efficiency of recovery and reuse of the extraction solvents.

To fully explore the utility of organosolv lignins, NREL intends to design and build an extraction device of suitable size to prepare between one and ten pounds of a low-molecular-weight fraction from a whole organosolv lignin. In addition, we are currently working with a commercial producer of organosolv pulp and lignin to obtain pulping liquor for evaluation as a source of lignin for catalyst synthesis.

Catalyst Production. The results of our research program has shown that each step of the lignin-to-catalyst process is chemically feasible, using low cost reagents and conditions.[7-11] However, several areas still need to be addressed; these include: improving the yield of the oxidation of lignin to benzoquinones, optimizing the Diels-Alder conditions, completing a set of synthesis steps with moderate amounts of materials, and testing the catalyst mixture for pulping activity.

1) A scaled up experiment will be carried through using the best conditions to date. The results of the experiment will be used as a basis for further process improvements and to update economic evaluations. The steps consist of:

a) a low-molecular-weight lignin NO_2 oxidation,
b) without purification, or with minimum purification, the NO_2 oxidation product will be treated with a diene,
c) the resulting product will be tested for catalytic pulping activity, and
d) the products from each reaction in sequence will be analyzed as completely as possible by available spectroscopic techniques.

2) Process improvement chemistry will continue in the following areas:

a) Oxidation technology. Heteropoly anion catalyzed chemistry, both with peroxide and oxygen as cheap and clean oxidizing agents, as well as improvement of the NO_2 technology will be examined. Lignin structures will be correlated to product yields to guide scale up efforts. Studies of the conversion of more complex structures in lignin will be performed to optimize the overall yield of the process.

b) Byproducts. Examination of byproducts from lignin oxidation procedures will be assessed to determine the need and methodology for recovery of unreacted oxidant and methods to handle spent reagents. This information is important to the process economics.

c) Diels-Alder reaction. Continue emphasis will be placed on optimizing yields in water as the solvent. New Diels-Alder catalysts, based on titanium and ruthenium, will be synthesized and investigated as a means to improve yields in non aqueous solvents.

3) Other biomass will be investigated in the oxidation technology. The emphasis will remain on pulping byproducts; however, bleach plant byproducts (new waste minimization technology), wood pyrolysis products and select non-woody materials will be screened.

Some specific technical areas to be assessed include:

- evaluating conditions leading to complete oxidation of a lignin dimer,
- correlating lignin structure with reactivity towards oxidizing agents,
- improving MMBQ yields from softwood lignin oxidation by metal/H_2O_2,
- examining the potential of "early-stage" lignin, organosolv lignin phenolics, and bleach liquors for generating benzoquinones,
- examining reductive lignin fragmentation procedures to develop starting materials for the catalyst synthesis,
- determining the economically feasible of C-5 functionalization of lignin prior to oxidation, and
- developing methods for obtaining consistent high yields of aromatic components from the Diels-Alder reactions.

Catalyst Performance. Pulping with AQ is a well studied process. However, the catalysts from our process will be part of a quinone containing mixture, which may include substituted AQ, AQ precursors, and unreacted low-molecular-weight lignin. The catalysts mixtures, prepared using the best synthetic routes, will first be evaluated for their ability to catalyze pulping on a small scale. Rate efficiencies of the mixtures will be determined. The best catalyst mixtures will then be tested on larger scale so that evaluation of the pulp quality and ease of chemical recovery from these liquors can be determined.

Work will be initiated on the detailed compositional analysis of the catalyst mixture remaining on the pulps. Such analyses may be required for FDA approval of the new process; however, AQ is already an approved pulping catalyst, components in the mixture are closely related to AQ, and most of the catalyst components are burned in the chemical recovery cycle.

The pulps will also be analyzed for normal strength properties, and, importantly, their bleachability. The bleaching tests will be carried out with different bleaching strategies: sequences that have chlorine-containing agents (principally chlorine dioxide) and others which do not. The latter bleaching strategy will lead to substantial environmental benefits by giving both a sulfur-free and chlorine-free pulp.

The spent pulping liquors will be evaluated, initially at a small scale. The recovery of these liquors will be similar to the recovery of a soda liquor; substantial energy and cost savings are expected compared to the conventional kraft process. For example, if a fluidized-bed combustion process can be combined with autocausticizing technology, a major reduction in capital cost of recovery will be obtained.

The technical areas to be assessed in this portion of the research include:

- pulping studies to define appropriate catalyst levels and strength parameters of the resulting pulp,
- bleaching studies to define the amounts and types of bleaching chemicals that are required for these pulps,
- developing chemical recovery technologies that compliment the less complex chemical system and contribute to the cost savings, and
- analyzing pulps for residual catalysts.

At this point, a more complete comparative technoeconomic analysis will be carried out based on these experimental results and performance of the operation at a small scale. These data will substantiate the projected energy and cost savings and provide the industry with the necessary information before investment in a pilot facility. The overall process will then be defined, and will underscore low overall emissions to air or waste water streams.

Catalyst Scale Up. As the program proceeds, the most promising technology for chemical processing of the low-molecular-weight lignin will be scaled to a larger size. The objective is to prepare between 0.5 and 5 lb. of pulping catalyst from low-molecular-weight lignin using this technology and to estimate the cost of producing this level of material as a guide to future scale up costs. The following areas will be considered:

- equipment design for scale up of the lignin isolation and chemical steps,
- the effect of scale up on product yields, quality, and distribution, and
- the economic feasibility of the different technologies.

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FUNDAMENTALS OF BLEACHING CHEMISTRY

PROJECT 3728

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ANNUAL RESEARCH REVIEW
APRIL 28, 1993

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
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TECHNICAL PROGRAM REVIEW FORM

PROJECT TITLE: FUNDAMENTALS OF BLEACHING CHEMISTRY

PROJECT STAFF: L.B. Sonnenberg, A.J. Ragauskas, D.R. Dimmel

FY 93-94 BUDGET: $195,000

REPORTING PERIOD: July 1992 - Feb.1993

DIVISION: Chemical and Biological Sciences

PROJECT NUMBER: 3728

OBJECTIVE: Provide a fundamental understanding of the physical and chemical reactions that control lignin removal and residual lignin structure. Understand the reasons for selectivity of reactions that occur in selected bleaching sequences.

IPST GOAL: Improved bleaching processes

SUMMARY:

Interest in developing nonchlorine bleaching techniques continues to grow in response to changes in the marketplace and proposed changes in environmental regulations. The wood chemistry group at IPST is currently engaged in investigations into the fundamental chemistry and the effectiveness of dimethyldioxirane (DMD), xylanase, and ozone.

The bleaching efficiency of DMD was explored for softwood kraft pulps. Preliminary studies demonstrated that kraft pulps could be delignified with DMD. Initial bleaching studies employed DMD prepared by distillation or in-situ from peroxymonosulfate, acetone, water and sodium bicarbonate. Further studies established that the bleaching reagents could be premixed and added to pulp to afford a comparable bleaching result.

Xylanase pretreatment was found to enhance the bleaching efficiency of several oxygen-based reagents: performic acid, peracetic acid, and ozone. Bleaching was evaluated by physical analysis (kappa, brightness, and viscosity) of the pulps after bleaching and caustic extraction. A xylanase pretreatment has the potential of reducing AOX formation and raising the brightness ceiling of fully-bleached pulps.

Ozone is a growing alternative to chlorine-containing bleaching reagents. Information about major by-products from pulp ozonation and residual lignin structure can provide useful information about many aspects of this new bleaching technology. Previous work is reviewed and recent results from studies of lignin ozonolysis by-products are reported.

Previous work at IPST determined that pulp ozonation produces basically two types of byproducts. One type consists of small, gas chromatographable compounds which are primarily fatty acids, short-chain and long-chain aliphatic acids and diacids. The precursors of some of the aliphatic acids and diacids are unsaturated fatty acids. Few monomeric lignin compounds are produced or survive ozonation. Evidence of lignin ozonolysis rests primarily in the presence of oxalic acid and glyoxylic acid (and/or their methyl esters). The other type of ozonation byproduct is methanol-soluble, water-insoluble, and possibly is composed of large, polar lignin fragments.

Earlier work with lignin model compound ozonations under different conditions suggested that the pathway of lignin ozonolysis is affected by the presence of cotton linters, reducing efficiency and producing different byproducts. It appears that a major reaction of ozone with the model in all of the systems is simply cleavage of the the most substituted, free phenolic ring of the lignin dimer.

In current work, we have continued to characterize byproducts from pulp ozonation and have focused on the role of secondary reactions in pulp ozonation. Ozone reacts with alkali-soluble pulp components in the presence of lignin as shown by size exclusion chromatography; however, these reactions may not represent a significant ozone depletion mechanism. There is evidence that these alkali-soluble substrates are low molecular weight (< 1000 daltons).

Ozone delignification produces compounds of high molecular weight (> 1000 daltons) in alkaline filtrates. The TOC in effluents increases with kappa reduction of the pulp and most of the increase is in high molecular weight carbon; however, there is also a small increase in the amount of small molecular weight compounds.

The least oxidized filtrates were the alkali-soluble components of unbleached pulp and they exerted the strongest ozone demand of all the filtrates. The filtrates from the ozonated pulps were considerably less reactive toward ozone, consistent with higher concentrations of carbonyl groups and carboxyl groups in the fragments.

We are examining the changes in the structure of the soluble lignin fragments and residual lignin under various bleaching conditions to determine what structural features induce dissolution of ozonized lignin. In the future, we will investigate how lignin, carbohydrates, and reactive intermediates interact during pulp ozonation.

GENERAL INTRODUCTION:

Interest in developing nonchlorine bleaching techniques continues to grow in response to changes in the marketplace and proposed changes in environmental regulations. The wood chemistry group at IPST is currently engaged in investigations into the fundamental chemistry and the effectiveness of ozone, dimethyldioxirane (DMD), and xylanase as nonchlorine bleaching reagents. Previous work is reviewed and current work is reported in three separate sections pertaining to the three reagents, "Fundamentals of Pulp Ozonolysis", "Fundamental Studies of Dimethyldioxirane as a Bleaching Reagent for Kraft Pulps", and "Effect of Xylanase Pretreatment Procedures for Nonchlorine Bleaching".

FUNDAMENTALS OF PULP OZONOLYSIS

INTRODUCTION:

The paper industry is seriously considering ozone as an alternative to chlorine-containing bleaching reagents. Information about major by-products from pulp ozonation and residual lignin structure can provide useful information about many aspects of this new bleaching technology, including mechanisms of delignification, optimal conditions for high efficiency and high selectivity, and optimal placement of ozone in a bleaching sequence. Results from studies of ozonolysis by-products are reported.

PRIOR RESULTS:

Pulp Ozonolysis By-products

Pulp ozonation produces basically two types of by-products. One type consists of small, gas chromatographable compounds which are primarily fatty acids, short-chain and long-chain aliphatic acids and diacids. The other type is methanol-soluble, water-insoluble, and possibly is composed of large, polar lignin fragments.

The precursors of some of the aliphatic acids and diacids are unsaturated fatty acids. In particular, nonanedioic acid is an important product of fatty acid cleavage in ozonated pulps. Even though the contribution of aliphatic acids can be reduced by pre-extraction of the pulp with methylene chloride, complete removal of the fatty acids and their ozonolysis products cannot be effected by methods used in this study. Alkaline washes prior to ozonation do not change the distribution of major products relative to one another.

Few monomeric lignin compounds are produced or survive ozonation. Evidence of lignin ozonolysis rests primarily in the presence of oxalic acid and glyoxylic acid (and/or their methyl esters). These compounds are major chromatographable components of ozonation by-product mixtures, based on relative signal sizes in gas chromatograms. Glyoxylic acid is by far the most abundant aldehyde present. Derivatization methods show that glyoxal is another important carbonyl by-product. Low concentrations of these small, secondary reaction products may indicate efficient and selective ozonation.

Carbonyl compounds that are present in ozonated pulp in small quantities relative to glyoxylic acid (methyl ester) have precursors that resist extraction from pulp by methylene chloride. However, alkaline washing prior to ozonation reduces carbonyl compounds. These results suggests that the precursors to carbonyl compounds are polar. In addition, northwestern pulp produces more carbonyl compounds than the southern pulp. Oxygen delignification prior to ozonation does not appear to greatly affect the distribution of carbonyl compounds. .

Lignin Model Compound Ozonolyses

Preliminary lignin model compound ozonations under different conditions suggest that the pathway of lignin ozonolysis is affected by the presence of cotton linters. The lignin model used in these studies was a guaicyl dimer. The reactivity of the lignin model was shown to be greater when dissolved or when spiked onto cotton linters than when it is suspended in water. Better accessibility of the model to ozone may partially explain the greater degradation of the adsorbed or dissolved model than the suspended model. When cotton linters were present in lignin model ozonations, more small acids were produced which suggests that the linters' presence alters predominate chemical pathways. The products of the lignin model compound ozonated in the presence of linters more closely resembled the products found from pulp ozonations. More ozone was consumed (although the same amount was applied) to achieve the same level of lignin model compound degradation when linters were present than when they were absent.

It appears that a major reaction of ozone with the model in all of the systems is simply cleavage of the the most substituted, free phenolic ring of the lignin dimer. One of the major products found in all systems is a lactone. The phenolic ring is cleaved and the resulting carboxylic acid reacts with the hydroxyl on the beta carbon to form the lactone. Further or concurrent reaction produces several products arising from cleavage of the side chain at various sites while the least substituted ring remains intact.

RECENT RESULTS:

Pulp Ozonolysis By-products

Recent work has involved characterization of all components of an ozonation effluent to complement the previous investigation of the small molecular weight products. Size distributions of alkali-soluble byproducts and the ozone demand of effluents were determined. Emphasis was placed on determining the relative importance of secondary reactions. Secondary reactions are defined here as reactions of ozone with dissolved lignin fragments or carbohydrates. Presumably, more secondary reactions will produce more oxidized effluents with a higher proportion of low molecular weight material.

Effluents with a high ozone demand will have a higher potential for secondary reactions and may cause inefficient bleaching.

Size Exclusion Chromatography The size distributions of the soluble lignin fragments in the alkaline rinsates of unbleached pulp and ozonated pulp were evaluated by size exclusion chromatography with ultraviolet detection. In Figure 1, the size exclusion chromatograms for the rinsates are shown at wavelenth 210 nm. There is a general increase in the intensity of most of the peaks as the ozone charge increases from 0.8 % to 1.4 % of ozone on o.d. pulp. The increase in peak intensities corresponds to a fairly linear increase in effluent total organic carbon and kappa reduction in the pulp (Figure 2).

Comparison of the chromatograms in Figure 1 shows that there are alkali-soluble components of the unbleached pulp that are removed during ozonation, suggesting that ozone is consumed by secondary reactions. The major positive peak in the chromatogram of the unbleached pulp rinsates eluting at approximately 28 minutes and the negative peak at approximately 40 minutes both decrease in intensity with ozone charge. Interestingly, the removal of these compounds does not correspond to a rise of any discernible, unique peak that may represent the ozonation products of the soluble components. It should be noted that the sharp positive peak at approximately 10 minutes may be an artifact of the sample work up procedure.

Negative peaks indicate the elution of compounds that absorb less than the mobile phase. These types of signals tend to be prevalent when wavelenths are monitored at which numerous compounds strongly absorb. Although the 210 wavelength tends to be noisy, it is also sensitive to many compounds that would not be detected at other wavelengths. Examples are given in Figure 3 of the size exclusion chromatograms generated at 254 nm, a wavelength commonly used to monitor unsaturation. The differences between the ozone effluents generated at different ozone charges are not apparent at this wavelength. The detectability, or lack of detectability, is an important issue in size fractionation techniques.

Ultrafiltration A second method we used for examining the size distributions of solubilized lignin fragments was ultrafiltration. The components of dilute, ozone byproduct solutions were separated into low and high molecular weight fractions with the cutoff point at approximately 1,000 daltons. The distribution of the ozonation products at different ozone charges is shown in Figure 4. It may be important that the ultrafiltrations were conducted at near neutral pHs. Ionized compounds may tend to be retained to a greater degree than their molecular weight would dictate and therefore the higher molecular weight fraction may be slightly high.

It is clear that ozone delignification occurs primarily by production of compounds of high molecular weight. The bulk of the TOC increase occurs in the high molecular weight fraction. However, a closer look at the low molecular weight TOC (Figure 5) shows that there is also an increase in low molecular weight products with ozone charge which may occur either through secondary reactions or direct ozone reactions with lignin.

Comparing ultrafiltration results with size exclusion results suggests two possibilities for secondary reactions. One possibility is that secondary reactions indicated by the size exclusion chromatograms do not degrade high molecular weight compounds (MW > 1000) to low molecular weight compounds (MW < 1000). In order to determine if the high molecular weight material in effluents from different ozone charges were similar, size exclusion chromatograms were generated for the UF retentates, i.e., the high molecular weight material (Figure 5). The similarity between the chromatograms for 0.8% and 1.4% ozone charge effluents suggests that the secondary reactions of alkali-soluble components of unbleached pulp must not involve high molecular weight material but must consist of low molecular weight material being degraded to lower still molecular weight material. The ultrafiltration filtrates were not analyzed by SEC because of sensitivity limitations.

There is a second possibility regarding the disappearance of UV-detectable byproducts with increasing ozone charge. Despite the detection of these changes by UV, the amount of material reacting in secondary reactions may not be significant compared to the amount removed from the pulp. As a result, there may be no significant increase in the proportion of low molecular weight material with increasing ozone charge.

The ozonolysis of extractives, which was shown to occur readily in earlier work on small molecular weight products, is consistent with many of these findings. The role of extractives in the effluent characteristics is currently under investigation.

Ozone Demand The ozone demand of ozonation effluents was also measured to determine the potential for secondary reactions (Table 1). The alkaline rinsate from the unbleached pulp exerted a strong ozone demand per gram of carbon in the rinsate, reflecting the relatively unoxidized state of the alkali-soluble pulp component. By contrast, the ozone filtrates have low ozone demands, consistent with the high oxidation state of the primary ozone products. Kamyr has also recently reported that the reactivity of ozone with carryover from cooking, oxygen delignification, peroxide, and ozone decrease in that order (Szopinski and Stromberg, 1993). The molar ozone consumption in our work was comparable to values reported by the Austrians for ozone consumption by liquor carryover in the Eo/pZP bleaching of sulfite pulp: 3 kg ozone is consumed per kg TOC in the carryover, which corresponds to a 0.08 ozone : carbon molar ratio (Peter and Ekholm, 1993).

There is some disparity in the results of studies of carryover effects. Lindholm (1988) found that ozonation filtrates used for low consistency ozone bleaching had no effect bleachability, except an increase in selectivity. Szopinsky et al (1993) have also found no consumption of ozone by Z stage filtrate components. However, Coledette et al. (1993) have found that Z stage filtrates reduce effiency while selectivity remains the same.

An important variable in ozone consumption by filtrates is likely to be the oxidation state of the filtrate components. The oxidation state will depend not only on the oxidant used to generate the filtrates, but also on the charges of the oxidants used, pH and other reaction variables. The importance of secondary reactions will depend on the relative extents of oxidation of the effluent and the pulp components. Presumably, the more soluble effluent components have a higher oxidation state and would therefore be less reactive toward ozone than pulp components. To investigate further, we are measuring the relative abundances of carbonyls, carboxylic acids, and hydroxyl groups in the ozonized pulp and in the soluble byproducts.

Conclusions Ozone reacts with alkali-soluble pulp components in the presence of lignin as shown by size exclusion chromatography; however, these reactions may not represent a significant ozone depletion mechanism. There is evidence that these alkali-soluble substrates are low molecular weight (< 1000 daltons).

Ozone delignification produces primarily of high molecular weight (> 1000 daltons) soluble byproducts. The increase in TOC in effluents from increasingly ozonized pulps occurs in the high molecular weight fraction; however, there is also a small increase in the amount of small molecular weight compounds.

The least oxidized filtrates were from the unbleached pulps and they exerted the strongest ozone demand. The filtrates from the ozonated pulps were considerably less reactive toward ozone, which likely due to higher levels of carbonyls and carboxyl groups in the soluble fragments.

Current Activity By examining the changes in the structure of the lignin fragments under various bleaching conditions, we plan to determine what structural features induce dissolution of ozonized lignin. The size of lignin ozonolysis products and the introduction of hydrophilic groups govern delignification. Therefore, we are analyzing pulp ozonation by-products for functional groups and size distributions under different conditions of carryover, charge, initial kappa number, and extractives' presence.

The residual lignin structure after ozonation is also under investigation. Other research into the production of small molecular weight ozone byproducts includes measurement of oxalic acid, formaldehyde and other carbonyl compounds.

In the future, we will investigate the role of carbohydrates in lignin ozonolyses. The course of the lignin reactions and the effect on carbohydrate structure will be examined through the use of several lignin derivatives, including lignin-carbohydrate complexes. We will attempt to identify reactive lignin intermediates and determine any reactions they may have with carbohydrates.

EXPERIMENTAL:

Ozone Ozonation of southern pine kraft pulp (kappa = 27.9) was carried out in a modified rotoevaporator apparatus at high consistency and at pH 2. Ozone was generated by a Welsbach Ozone Generator. The three ozonized pulps consumed 0.8 %, 1.0 % and 1.4% ozone on o.d. pulp. Effluents were generated by thoroughly rinsing ozonated pulp with an alkaline solution composed of 0.02 M NaHCO3, 0.01 M NaCl, and enough NaOH to adjust the pH to 10.5. The solution composition was selected on the basis of optimizing size exclusion analyses.

Size exclusion chromatography Size exclusion chromatography was conducted on an HP 1090 liquid chromatograph equipped with a photodiode array detector (several wavelengths were monitored) and a TSK-Gel PW 4000 column (Toyapearl). A typical mobile phase was 0.02 M NaHCO3, 0.01 M NaCl and NaOH to pH = 10.5. No improvements in chromatography were obtained by adding polyethylene glycol or methanol to the mobile phase or altering its pH.

Ultrafiltration An Amicon 250 mL ultrafiltration unit equipped with a UM2 membrane (MW cutoff ≈ 1000) was used. Samples were diluted 100-fold prior to diafiltration in order to minimize aggregation effects. Diafiltration is the displacement of sample solvent with fresh solvent while maintaining a constant volume. The sample solvent volume turned over approximately 50-60 times.

Ozone demand The values for ozone demand are operationally defined. In these experiments, ozone was bubbled through acidified effluents at a constant rate (50 mg O3/ min) for 2 minutes. The amount of ozone delivered and the amount remaining after exposure to the effluent were measured by iodometric titration of potassium iodide traps.

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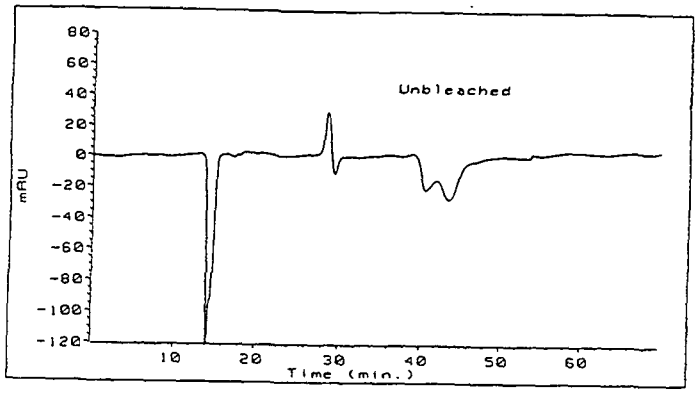
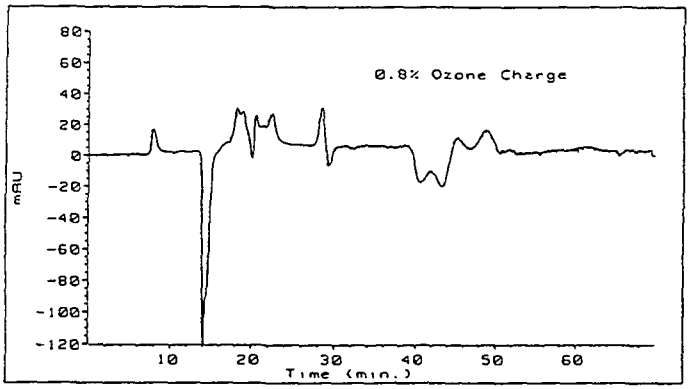
Table 1. Total Organic Carbon and Ozone Demand of Whole Ozone Effluents and the High Molecular Weight Fraction of Effluents

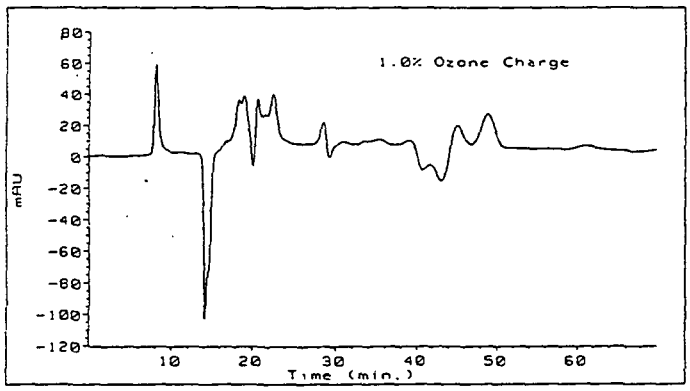
Ozone Charge, % on o.d. pulp	Whole Effluents mg C/ g pulp [a]	Retentates (HMW) mg C/ g pulp [a]	Whole Effluents mol O_3/ mol C [b]	Retentates (HMW) mol O_3/ mol C [b]
0.0	0.8	0.3	0.7	0.9
0.8	5.1	2.8	0.1	0.1
1.0	6.7	4.2	0.1	<0.1
1.4	8.6	5.8	0.2	0.1

a Milligrams of soluble carbon produced per gram of pulp ozonated.
b Moles of ozone consumed per mole of carbon in each effluent.

Figure 1. **Size Exclusion Chromatograms of Alkali-Soluble Pulp Ozonolysis Products (210 nm)**







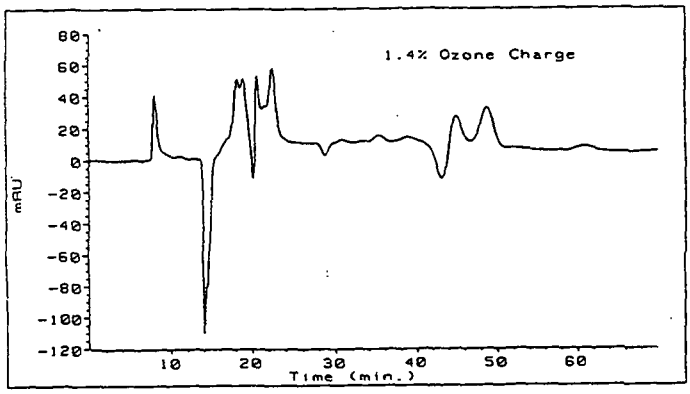


Figure 2. **Kappa Numbers of Ozonized Pulp and Soluble Organic Carbon in Alkaline Filtrates**

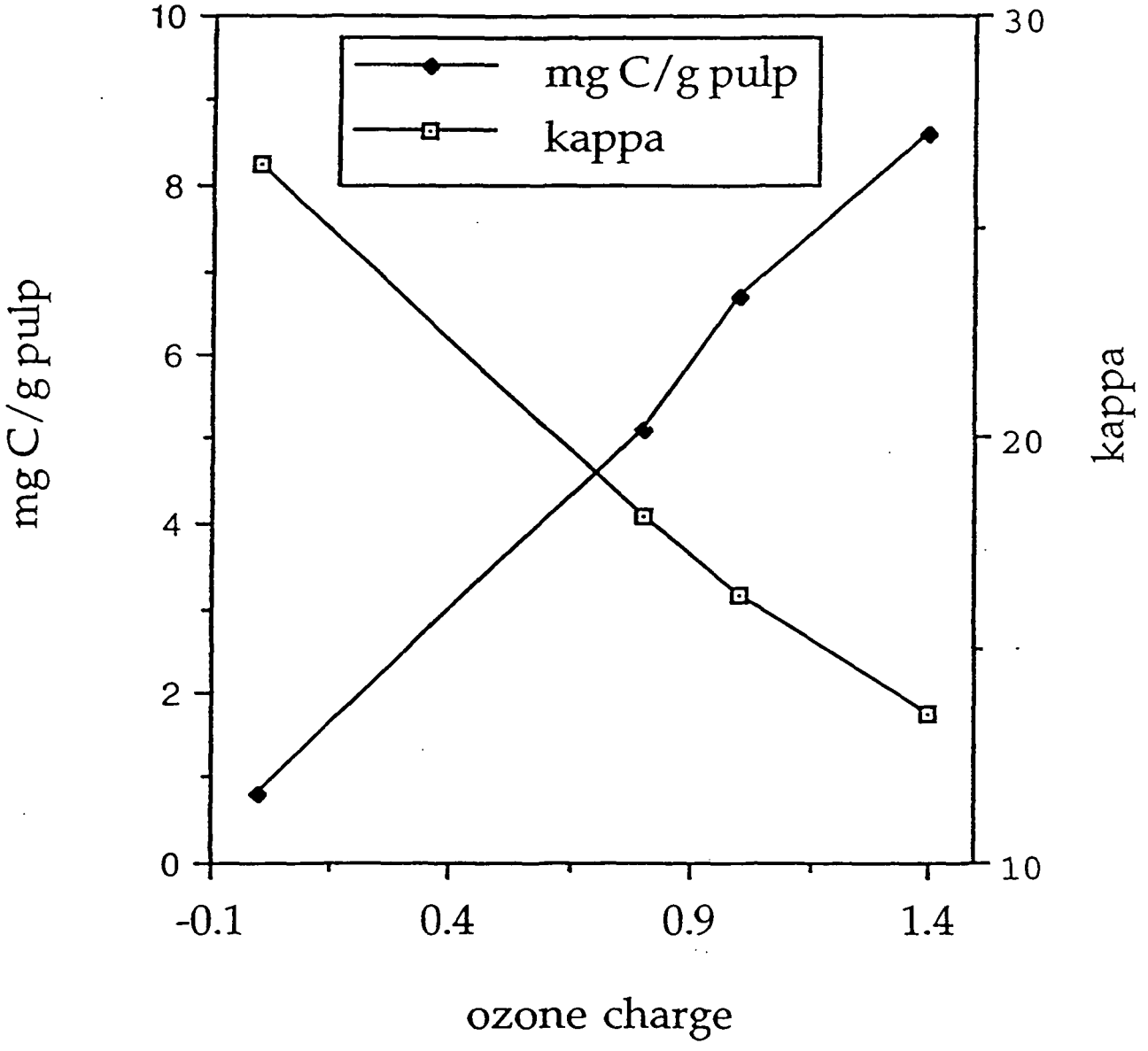
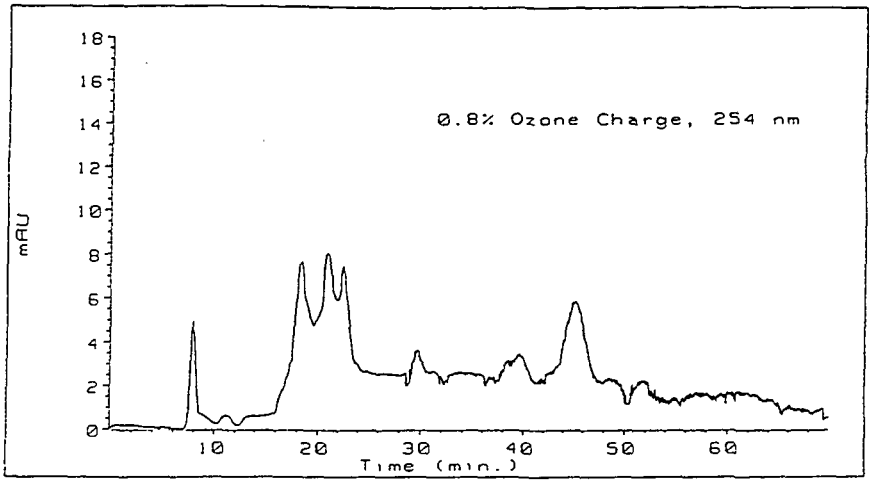
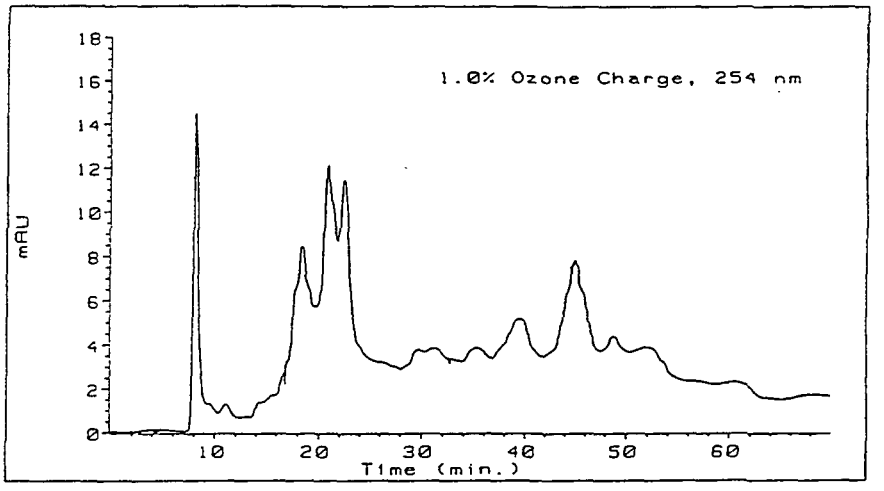


Figure 3. Size Exclusion Chromatograms of Alkali-Soluble Pulp Ozonolysis Products (254 nm)





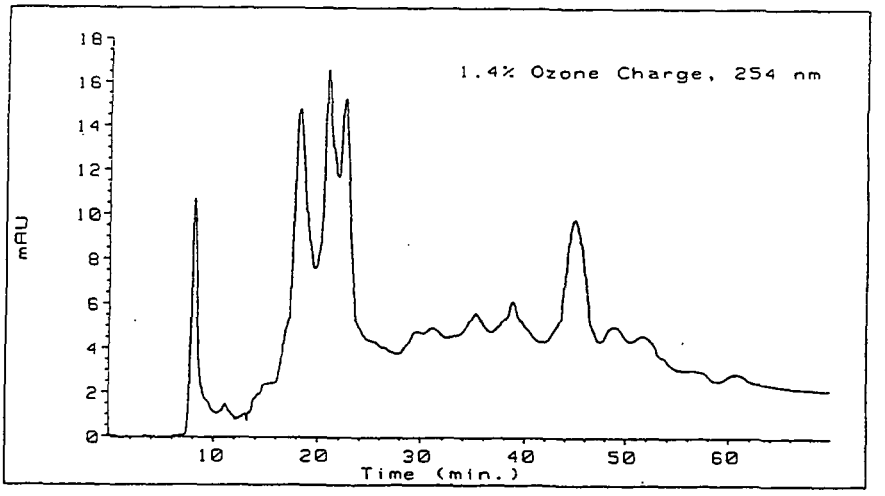


Figure 4. **Size Distributions of Alkali-Soluble Pulp Ozonolysis Products Based on Ultrafiltration**

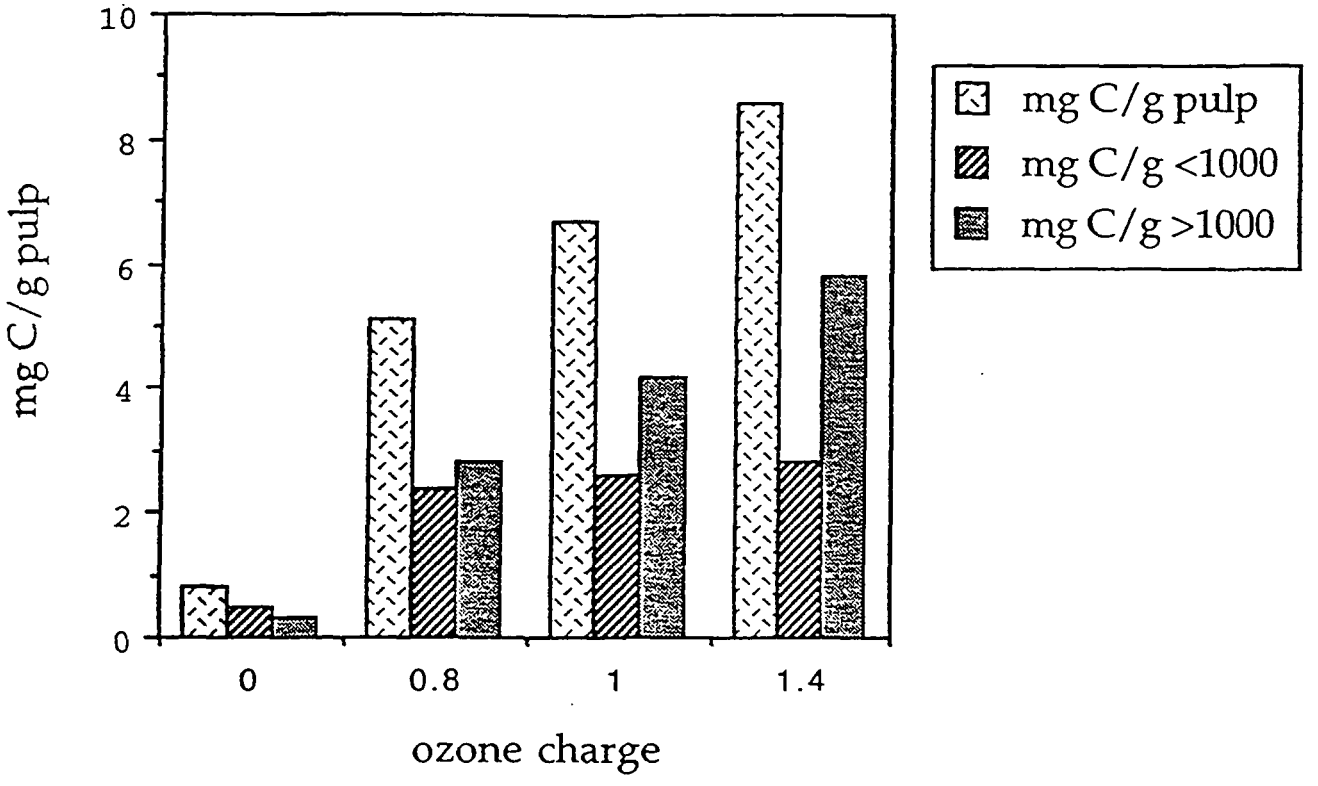
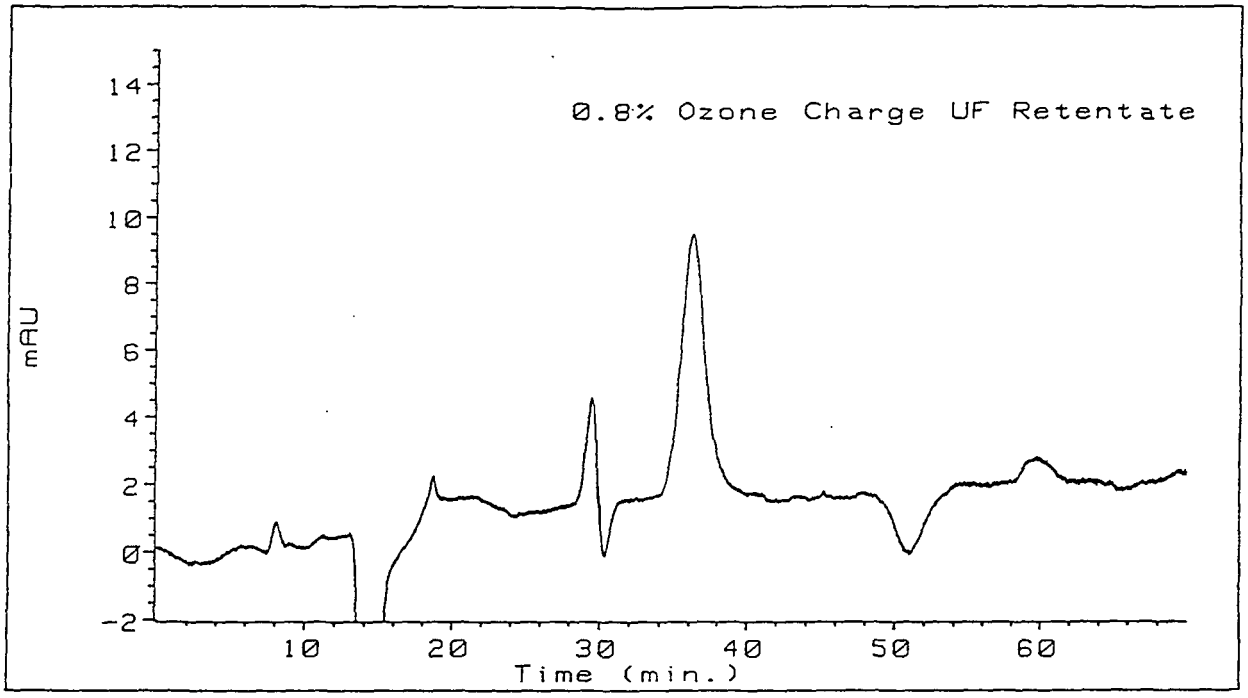
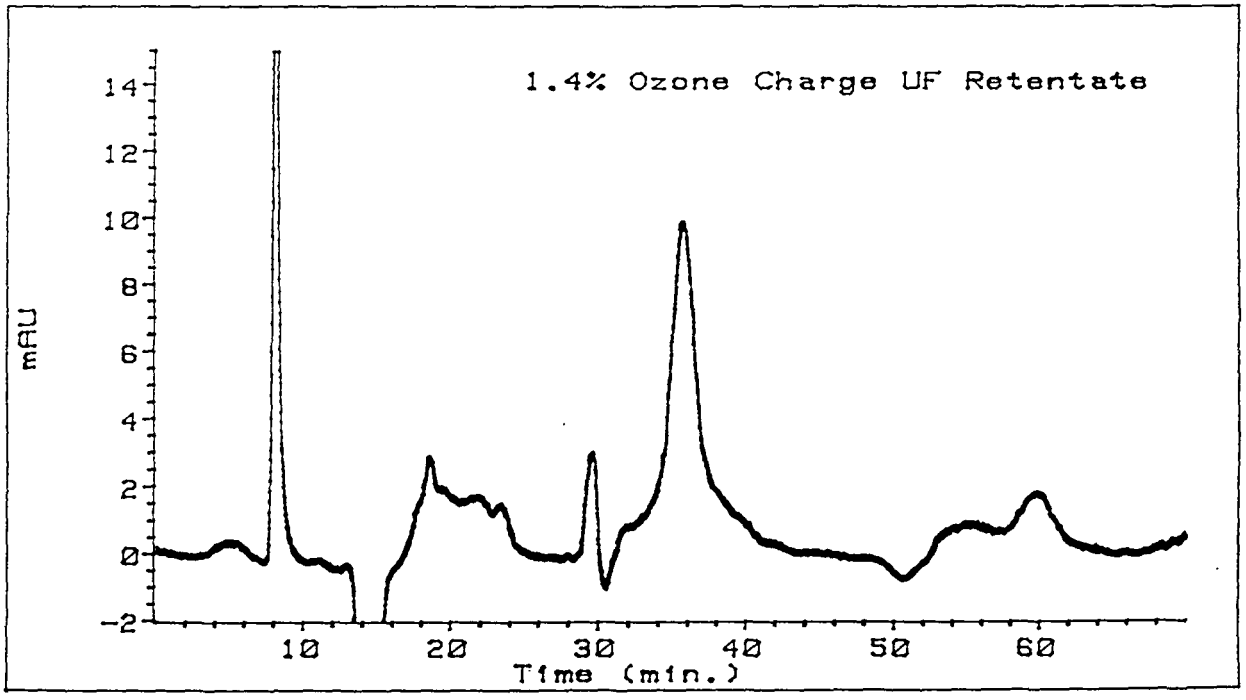


Figure 5. Size Exclusion Chromatograms of Ultrafiltration Retentates (210 nm)





SECTION 1

FUNDAMENTAL STUDIES OF DIMETHYLDIOXIRANE AS A BLEACHING REAGENT FOR KRAFT PULPS

Dr. Arthur J. Ragauskas

Fundamental Studies of Dimethyldioxirane as a Bleaching Reagent for Kraft Pulps

INTRODUCTION

Interest in developing new alternative methods for bleaching kraft pulps continues to grow in response to changes in the marketplace and proposed changes in environmental regulations. Although no one bleaching reagent has been shown to be as efficient as chlorine many alternative chemical and biological processes are under active investigation. In light of the growing interest in the field of bleaching technology, research efforts in the wood chemistry group at IPST have been directed at developing novel oxidants for bleaching kraft pulps. To date, one of the most successful reagents we have studied is dimethyldioxirane. Previous studies, summarized in last year's PAC report, demonstrated that this reagent possesses unique bleaching capabilities. Research efforts in this area have continued with an emphasis on enhancing the bleaching efficiency of this reagent and examining the chemical effects that this reagent has on kraft pulps.

RESULTS AND DISCUSSION

Xylanase/DMD: Last year's preliminary studies clearly suggested that the strained cyclic structure of dimethyldioxirane (DMD) is an exceptionally reactive peroxide with unique bleaching properties. As summarized in Table 1, treatment of kraft pulps with dimethyldioxirane was shown to significantly reduce the kappa number and raise the brightness values for the bleached pulps. Subsequent caustic extraction removed additional lignin and further increased the brightness of the resulting pulp. To further enhance the bleaching efficiency of DMD we explored the compatibility of this bleaching reagent with xylanase biobleaching pretreatment regimes. The pretreatment of kraft pulps with xylanase has been shown to have several beneficial effects for chlorine/chlorine dioxide bleaching[1] and by extension we had anticipated the bioboosting effect of this enzyme pretreatment procedure could enhance the bleaching efficiency of dimethyldioxirane.

To explore the synergistic effects between xylanase and dimethyldioxirane we pretreated kraft hardwood and softwood pulps with xylanase,[1] bleached with a 0.5% charge of DMD, and then extracted with caustic. The effect of xylanase pretreatment on the bleaching efficiency of DMD was evaluated through a series of control experiments for which the biobleaching procedure was omitted. The results of these studies are summarized in Tables 2 and 3. A comparison of the bleaching data for the hardwood kraft pulps indicates that the xylanase pretreatment procedure enhances the delignification and bleaching efficiency of DMD while maintaining good viscosity values. Xylanase pretreatment of softwood kraft pulps enhanced the bleaching efficiency of DMD, as measured by extent of delignification and changes in viscosity, although the results were not as significant as for the hardwood pulps. Presumably, the hardwood pulps exhibited

a superior response to xylanase pretreatment regimes due to their higher xylan content. Nonetheless, these results suggest that pretreatment of kraft pulps with xylanase provides an effective method of enhancing the bleaching efficiency of DMD.

Characterization of DMD Treated Pulps: Preliminary studies were initiated to characterize the effect that DMD bleaching has on the chemical structure of residual lignin. The goal of these studies was to determine what occurs to the methoxy, phenoxy, and carboxylic acid content of DMD treated pulps. These results will be compared against pulps treated with comparable amounts of Caro's acid. It is anticipated that as our understanding of DMD bleaching chemistry advances it may be possible to develop the optimal bleaching sequence for this reagent or alternatively, novel methods of bleaching kraft pulps may also be discovered.

In this report we will summarize the results of our studies directed at examining the changes in methoxy content upon bleaching with DMD or Caro's acid. Employing an 8% charge of $KHO_2SO_3 \bullet KHSO_4 \bullet K_2SO_4$, DMD was generated in-situ following the optimized procedure developed in the 1992-93 PAC research program. The in-situ generated DMD was then applied onto a commercial softwood kraft pulp (kappa # 22.0), stirred for one hour and then extracted. The control experiment employed the same reagents except acetone was omitted from the mixture, therefore the active reagent was Caro's acid. After bleaching and caustic extraction pulp samples were analyzed for % methoxyl content, following well established literature procedures.[2] The results of these studies are summarized in Table 4. Although the results do not differ greatly for either the DMD or Caro's acid treated pulps the data indicates that after caustic extraction DMD treated pulps, are not significantly altered with regard to methoxyl content. The results for phenoxyl and carboxylic acid content are on-going and will be completed shortly.

CONCLUSIONS AND FUTURE RESEARCH

Dimethyldioxirane has been shown to be a very efficient and selective bleaching reagent for kraft pulps. Furthermore, the application of this reagent in conjunction with xylanase pretreatment procedures further enhances the bleaching efficiency of this reagent. Research studies are ongoing to evaluate the impact of a xylanase/DMD bleaching procedure for fully bleached pulp.

Planned future research efforts include: employing H_2O_2/H_2SO_4 as a source of Caro's acid for generating DMD; employing reagents other than acetone to generate alternative dioxirane structures; developing truly catalytic dioxirane bleaching systems; and studying appropriate bleaching sequences for dioxirane reagents.

External funding for these studies has been secured and future research efforts will be sponsored principally by these sources.

ACKNOWLEDGEMENTS

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Table 1. Effects of a 5% Charge of Dimethyldioxirane[a] on Kraft Pulps

Pulp	Initial		Bleached[b]		Extracted[c]	
	Kappa #	Brightness[d]	Kappa #	Brightness[d]	Kappa #	Brightness[d]
Softwood[e]	39.5	23.1	12.5	31.4	11.9	34.0
Softwood[e]	27.6	20.5	11.1	30.2	8.5	32.7
Hardwood[e]	11.5	29.7	--	--	2.6	44.2

[a]applied as a freshly distilled solution of 0.1 N DMD in acetone; [b]kraft pulp (5% consistency) was treated with DMD for 1 h at RT; [c]DMD bleached kraft pulp extracted with an aqueous 1.5% NaOH solution for 3/4 h; [d]Tappi standard[3]; [e]bleaching studies employed industrial, never-dried southern softwood and northern hardwood kraft pulps.

Table 2. Characterization of Xylanase Biobleaching Effects on Dimethyldioxirane Bleaching of Kraft Hardwood Pulp

	Pulp Properties		
Pulp	Kappa	Viscosity/Cp.	ISO Brightness
Brownstock[a]			
-Untreated	18.0	49.5	34.7
-Enzyme Treated[b]	17.3	51.0	35.1
Bleached with 0.5% Dimethyldioxirane			
-Untreated	14.0	48.7	--
-Enzyme Treated[b]	11.9	51.0	--
Bleached with 0.5% Dimethyldioxirane followed by caustic extraction[c]			
-Untreated	12.7	38.5	42.9
-Enzyme Treated[b]	10.7	41.6	45.5

[a]bleaching studies employed an industrial, never-dried northern hardwood kraft pulp; [c]the pulp samples were bleached with dimethyldioxirane at low consistency for 1 h. After bleaching, the pulp was washed with water and extracted with a 1.5% NaOH solution for 1 h. The reported physical data were determined after washing the bleached, caustic extracted pulp; [b]pulp samples were treated with xylanase following literature procedures.[1]

Table 3. Characterization of Xylanase Biobleaching Effects on Dimethyldioxirane Bleaching of Kraft Softwood Pulp

	Pulp Properties		
Pulp	Kappa	Viscosity/Cp.	ISO Brightness
Brownstock[a]			
-Untreated	27.4	37.0	29.7
-Enzyme Treated[b]	26.7	38.5	30.6
Bleached with 0.5% Dimethyldioxirane			
-Untreated	26.2	35	--
-Enzyme Treated[b]	23.1	36.6	--
Bleached with 0.5% Dimethyldioxirane followed by caustic extraction[c]			
-Untreated	23.3	31.7	31.4
-Enzyme Treated[b]	22.7	32.3	31.2

[a]bleaching studies employed an industrial, never-dried northern softwood kraft pulp; [b,c]see footnotes in Table 2.

Table 4 Methoxyl Content of Caro's Acid and DMD Treated Softwood Kraft Pulp[a]

Pulp	Initial	4% Caro's Acid[b]		4% Caro's Acid/Acetone[c]	
		Bleached	Extracted[d]	Bleached	Extracted[d]
Kappa #[e]	22.0	19.7	19.2	17.91	16.1
% Methoxyl on Solids[f]	0.51	0.51	0.47	0.49	0.49

[a]bleaching studies employed industrial, never-dried southern softwood kraft pulps; [b]wt of Caro's acid/wt of pulp, bleaching studies were performed at 5% consistency and at RT; [c]DMD was generated in-situ followed by premixing oxone with acetone, as described in last years PAC report; [d]bleached kraft pulp was extracted with an aqueous 1.5% NaOH solution for 3/4 h at RT; [e]Tappi standard[3]; [f]see reference 2.

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3. a) TAPPI testing methods T236.
   b) TAPPI testing methods T230.
   c) TAPPI testing methods T452.

SECTION 2

EFFECT OF XYLANASE PRETREATMENT PROCEDURES FOR NONCHLORINE BLEACHING

Dr. Arthur J. Ragauskas

Effect of Xylanase Pretreatment Procedures for Nonchlorine Bleaching

INTRODUCTION

Advances in the application of biotechnology to the pulp and paper industry have developed significantly over the past few years.[1] To date, one of the most successful applications has been the use of *endo*-(1,4)-β-D-xylanase as a pretreatment for chlorine and chlorine dioxide bleaching sequences.[2] Based on numerous laboratory[3] and mill studies,[4] it is now becoming well established that pretreatment of kraft pulps with xylanase significantly enhances the bleachability of these pulps for chlorine-based bleaching sequences such as (CD)EDED[5] or DEDED (C:chlorine; D:chlorine dioxide; E: caustic extraction; see Table 1 for a complete listing of bleaching abbreviations). The most significant bleaching benefits found from xylanase pretreatment regimes includes higher brightness ceilings, reductions in the amounts of bleaching chemicals needed to achieve high brightness, and reduced amounts of organo-chlorine compounds in bleach plant effluents. In addition, all of these benefits are incurred without significant capital costs or changes in the bleaching process.

The pretreatment of kraft pulps with xylanase followed by high chlorine dioxide substitution in the early stages of pulp bleaching provides a facile method of addressing current environmental concerns. Nonetheless, it remains uncertain if these practices will be acceptable in the future as more stringent environmental regulations are drafted. In response to these environmental concerns, a variety of nonchlorine bleaching procedures are being investigated. In this study, we have examined the effect of xylanase pretreatment on bleaching efficiency for a variety of non-chlorine based bleaching reagents, including performic acid, peracetic acid, peroxymonosulfate acid, and ozone. All of these reagents are under active investigation as possible bleaching chemicals for non-chlorine bleaching of kraft pulps and could potentially benefit from a xylanase pretreatment procedure.

MATERIALS AND METHODS

Materials

Hydrogen peroxide (30% by wt.), formic acid, peracetic acid (32% by wt), and the triple salt of $KOSO_4 \bullet KHSO_4 \bullet K_2SO_4$ (trade name, Oxone™) were commercially purchased and used without further purification. Commercial xylanase was kindly provided by ICI Biological Products. Xylanase activity was determined as reducing sugars released from the water-soluble portion of oat-spelt xylan (1%) following Miller's procedure.[6] Bleaching studies employed industrial, never-dried, softwood kraft pulp (Kappa number 23.0). Prior to bleaching and/or enzyme treatment the extractives from the pulp were removed following TAPPI method T264. The extractives were removed from the pulp to simplify subsequent effluent characterization studies which are on-going.

Xylanase Treatment of Pulps

All xylanase treatments were carried out on 88 gr batches of extractives-free, softwood kraft pulp (Kappa number 22.3) at 6% consistency. Prior to addition of the enzyme the pulp slurry pH was adjusted to ca 5.5-6.0 with 1 M H_2SO_4. Enzyme was added at a dose of 7,480 IU (2.75 ml, xylanase activity/ml: 2,713 IU/ml) to the pulp slurry and then sealed in a polyethylene bag. This mixture was immersed in a constant temperature bath (50°C) for 2 h. During the xylanase pretreatment reaction the pulp sample was kneaded every 15 min to ensure uniform distribution of the enzyme. The pulp was then washed with water and suction dried to approximately 15% consistency. The xylanase treated pulps were immediately bleached or stored at 4° C for no longer than one week.

Physical & Chemical Characterization of Pulps

The Kappa number was determined by $KMnO_4$ titration of the pulp following standard Tappi method T-236. Brightness values for the pulp samples were measured by preparing optical handsheets (TAPPI standard method T-218) and measuring the percent light reflectance at 457 nm following Tappi method T-452 and/or T-534. The viscosity of the pulp was measured employing a capillary viscometer as described in Tappi method T-230.

Bleaching Procedures

Bleaching Conditions for Oxone, Performic Acid and Peracetic Acid

Prior to bleaching with either performic acid or peracetic acid the pulps were treated with acetic acid following Sundquist's procedure[7] for removing trace metals. The pulp samples bleached with oxone were first treated with Na_2SO_3 and DTPA (0.4% charge) to remove trace metals.

Pulp samples (25 g, OD:oven-dry weight) were placed in a polyethylene bag containing water and a stabilizing reagent (see Table 2 for further detail). After thoroughly mixing the pulp by kneading, the pulp slurry was preheated to 70° C. The bleaching reagent was then rapidly added to the pulp and the sample bag was sealed, kneaded, and then immersed in a constant temperature water bath. During the bleaching reaction the pulp sample was kneaded every 15 min to ensure a uniform distribution of the bleaching reagent throughout the sample. Upon completion of the bleaching reaction the pulp was removed from the water bath and its contents were washed with distilled water (4 x 500 ml). The pulp was then suction dried and analyzed for lignin content (Kappa #), brightness, and viscosity.

A portion of the bleached pulp (12 g, OD) was then diluted with 0.12 N NaOH solution to 1% consistency, sealed in a polyethylene bag and warmed to 70° C for one hour. The extracted pulp was then filtered and washed with distilled water (4 x 500 ml).

Ozone Bleaching Conditions

Ozone bleaching studies were carried out at 30-35% consistency after prewashing the pulp with a 1 M H_2SO_4 solution. Pulp samples (50 gr, oven dry weight) were then treated with ozone by means of a modified roto-evaporator designed to deliver ozone directly onto the pulp. A Welsbach ozone generator was used to provide ozone/oxygen gas for each bleaching experiment. Ozone gas concentrations were monitored by measuring the concentration of ozone before and after contact with the pulp. Ozone concentrations were determined by bubbling the gas through an aqueous 10% KI solution and then titrating the solution with 0.10 N sodium thiosulfate solution. Detailed descriptions of the ozone bleaching experiments are summarized in Table 3.

RESULTS AND DISCUSSION

The effects of xylanase pretreatment on oxygen-based bleaching reagents was studied with a southern softwood kraft pulp. The pulp was pretreated with a xylanase, cellulase-negative solution following well established literature procedures.[2] As summarized in Table 4, treatment of the brownstock increased the viscosity and brightness of the pulp by 6% and 12% respectively. Enzyme treatment also removed minor amounts of lignin decreasing the kappa value of the pulp by 3%. The improvements in the viscosity presumably occur due to an enrichment in high molecular weight polysaccharides, which occurs when xylan is selectively removed. The gain in brightness and the loss of lignin after enzyme treatment has been previously noted in the literature and is attributed to the loss of lignin-carbohydrate complexes.[5]

Our initial bleaching studies focussed on evaluating the biobleaching effect on oxone,[8] peracetic acid,[9] and performic acid.[7] Following well established literature bleaching procedures for these reagents the control and xylanase-treated pulps were bleached and then extracted with 0.12 M NaOH solution. After caustic extraction the kappa number, viscosity, and brightness values were determined following standard procedures and these results are summarized in Table 4. The results of these studies indicated that the enzyme pretreatment procedure had no beneficial effects for performic acid bleaching. The results from the oxone bleaching reaction suggested a minor enhancement in the overall extent of lignin removal for the enzyme treated pulp.

The results of peracetic acid bleaching studies were of greater interest since the xylanase pretreatment procedure provided a significant biobleaching effect. As summarized in Table 4, depending upon the amount of peracetic acid employed during bleaching, the xylanase pretreated pulps exhibited a 0 - 7% additional loss in lignin while maintaining viscosities comparable to the control pulps. Furthermore, the enzyme treated pulps exhibited higher brightness values after bleaching and caustic extraction. The bioboosting effect of xylanase was most efficient with a low charge of lignin which could be attributed to the extent of lignin oxidation during bleaching. Since potential future bleaching applications of peracetic acid would employ relatively low charges of this reagent our

results clearly suggest that xylanase pretreatment could enhance the bleaching efficiency of peracetic acid.

The final bleaching reagent examined in this preliminary study was ozone. Due to current bleaching interests in this reagent we elected to monitor the bio-bleaching effect after ozone treatment and following caustic extraction. Prior to ozone bleaching the pulp samples were acidified to a pH of 5 or 2. At the latter pH two series of bleaching experiments were performed employing a 0.6% charge and a 1.2% charge of ozone. The pH 5 pulp sample was bleached with a 0.6% charge of ozone. Although it is well known that the optimal pH for ozone bleaching is between 2-3 we wished to determine if the xylanase pretreatment procedure could alter the preferred pH range for ozone bleaching.

The control and xylanase-treated pulps were bleached at high consistency in a modified roto-evaporator especially designed to maximize ozone contact with the pulp. The results of the ozone bleaching studies are summarized in Table 5 and this data demonstrates that xylanase pretreatment of the softwood kraft pulp impacts beneficially on delignification, brightness gains, and viscosity changes. Examination of the kappa numbers after bleaching and caustic extraction for the 0.6 and 1.2% charge of ozone (pH 2.5) reveals that the bioboosting effect of xylanase is not diminished with the larger charge of ozone. These results differ from the bleaching data obtained with peracetic acid, where the biobleaching effect was shown to be sensitive to the amount of reagent employed. A comparison of the ozone bleaching data acquired at a pH of 2.5 and 5.0 with a 0.6% charge of ozone suggests that the optimal pH range for ozone bleaching of xylanase treated pulps remains at a pH level of 2-3. Nonetheless even at this unfavorable pH of 5 the enzyme treated pulp responds more favorably to ozone.

CONCLUSIONS

In summary, these results demonstrate that xylanase pretreatment of softwood kraft pulps can enhance the bleaching efficiency of several non-chlorine based bleaching reagents including ozone. These studies suggest that the application of xylanase in the early stages of a bleaching sequence could reduce chemical consumption of oxygen-based bleaching reagents and enhance the physical performance of the fully bleached pulps.

Table 1: List of Bleaching Abbreviations

Abbreviation	Bleaching Reagent
C	Chlorine
DMD	Dimethyldioxirane
D	Chlorine Dioxide
E	Caustic Extraction
O	Oxygen Delignification
P	Hydrogen Peroxide
PFA	Performic Acid
PPA	Peracetic Acid
Z	Ozone
X	Pretreatment with Xylanase

Table 2: Bleaching Conditions Employed for Oxone, Performic, and Peracetic Acid Treatments of Softwood Kraft Pulp

Bleaching Reagent:	Oxone[a]	Performic Acid[b]		Peracetic Acid[c]		
Charge (gr/gr OD)	8%	3.9%	7.8%	2.0%	3.95	4.4%
Stabilizer Employed (gr/gr OD pulp)	--	2.5% Citric Acid		2.5% Citric Acid		
Bleaching Temperature (C)	70°	80°	80°	80°	80°	80°
Bleaching Time (hr)	1	3	3	3	3	3

[a]Hammann's bleaching procedure[8]; [b]performic acid was generated in-situ following the procedure described by Sundquist et. al.[7] employing a 50% formic acid bleaching solution; [c]employed commercial 32% by weight solution of peracetic acid in dilute acetic acid.

Table 3: Bleaching Conditions Employed for Ozone Treatments of Softwood Kraft Pulp

Bleaching Reaction	Charge of Ozone Applied to the Pulp	Initial pH of Pulp
I	1.2%	2.5
II	0.6%	2.5
III	0.6%	5.0

Table 4: Results from Bleaching Softwood Kraft Pulp with Oxone, Performic and Peracetic Acid Treatments of Softwood Kraft Pulp

Bleaching Treatment	Kappa	Tappi Brightness	Viscosity/cP
Brownstock	22.3	24.0	14.2
Xylanase-treated Brownstock	21.7	26.8	15.1
X(PFA-3.9% charge)E	14.3	--	--
(PFA-3.9% charge)E	14.0	--	--
X(PFA-7.8% charge)E	8.6	35.1	5.3
(PFA-7.8% charge)E	8.8	34.0	5.6
X(PAA-2.0% charge)E	7.2	51.4	7.6
(PAA-2.0% charge)E	8.8	49.4	7.8
X(PAA-3.9% charge)E	5.4	51.4	7.4
(PAA-3.9% charge)E	6.3	48.7	7.9
X(PAA-4.4% charge)E	5.8	51.2	8.9
(PAA-4.4% charge)E	6.2	49.8	8.5
X(Oxone-8%)E	14.1	29.0	9.5
(Oxone-8%)E	15.1	29.2	9.0

Table 5: Characterization of Xylanase Biobleaching Effects on Ozone Bleaching of Kraft Softwood Pulp

	Pulp Properties		
Pulp	Kappa	Viscosity/cP	Tappi Brightness
Brownstock	22.3	14.2	24
Xylanase treated brownstock	21.7	15.1	27
Bleached with 1.2% ozone/pH:2.5			
-Xylanase-treated	9.9	--	--
-Control	11.6	--	--
followed by caustic extraction[a]			
-Xylanase-treated	6.3	10.3	48
-Control	7.6	9.4	44
Bleached with 0.6% ozone/pH:2.5			
-Xylanase-treated	15.2	--	--
-Control	15.8	--	--
followed by caustic extraction[a]			
-Xylanase-treated	11.1	12.1	38
-control	12.5	11.4	36
Bleached with 0.6% ozone/pH:5.0			
-Xylanase-treated	15.0	--	--
-Control	16.1	--	--
followed by caustic extraction[a]			
-Xylanase-treated	12.2	12.2	36
-Control	13.9	11.7	32

[a]extracted with a 0.12 M NaOH solution for 1 h at 70°C.

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FUNDAMENTALS OF BRIGHTNESS STABILITY

PROJECT 3524

Arthur J. Ragauskas

ANNUAL RESEARCH REVIEW
APRIL 28, 1993

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
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TECHNICAL PROGRAM REVIEW REPORT

PROJECT TITLE: FUNDAMENTALS OF BRIGHTNESS STABILITY

PROJECT STAFF: A.J. Ragauskas

BUDGET (FY 92-93): $80,000

REPORTING PERIOD: April 1992 - February 1993

DIVISION: Chemical and Biological Sciences

PROJECT NUMBER: 3524

OBJECTIVE: Research activities are directed at investigating the fundamental chemical reactions which are initiated when high yield-pulps are photolyzed. As our knowledge of the photoxidation of mechanical pulp increases, methods to eliminate or significantly retard the yellowing process will be pursued.

IPST GOAL: Increase the usefulness of high-yield fibers.

SUMMARY OF RESEARCH ACCOMPLISHMENTS:

1991-92: As a result of an extensive survey of compounds, we discovered three new structurally related sets of additives which could retard relative rates of brightness reversion. The three types of additives contain the diene functionalities and can be classified as substituted 1,3- or 1,4-cyclohexadiene structures, derivatives of 1,4-pentadien-3-ol and substituted 2,4-hexadiene type systems. The most successful additive studied was trans,trans-2,4-hexadien-1-ol. Photo-reversion studies with BCTMP pulp samples treated with this alcohol demonstrated that this compound can photo-stabilize hardwood bleached chemithermalmechanical pulp (BCTMP) as effectively as ascorbic acid. Unfortunately, this reagent was shown to accelerate the long term thermal reversion properties of the handsheet.

The chemical mechanisms contributing to the photo-formation of chromophoric structures in mechanical pulp were also explored. Research efforts demonstrated that current lignin model compounds employed in the literature fail to yield *ortho*-quinone like structures. Since *ortho*-quinones have been detected in mechanical pulp these results indicate that the exact chemical mechanisms involved in oxidizing phenolic structures in lignin to quinones is far from understood.

Finally, the photo-reactivity of chromophoric structures commonly believed to contribute to yellowing were studied. Employing a series of *para*- and *ortho*-quinone structures, we established that most quinone structures do not contribute to further photochemical yellowing of mechanical pulp. Research efforts have also demonstrated that hydroxy-*para*-quinones exhibit chemical behavior analogous to that of *ortho*-quinones.

1992-93: Research efforts over the last fiscal year have focused on three important aspects of the brightness reversion phenomenon: the design of novel photostabilization techniques and reagents; investigating the fundamental chemistry of known photo-stabilization techniques; and examining the performance of photo-stabilization reagents over extended periods of storage. These studies have lead to several significant advances, including:

- Identification of β-diketones as potential photo-stabilizers for mechanical pulp;
- Establishment of physical requirements for efficient stabilization of high-yield pulps;
- Investigation of the mechanism of thiol-stabilization of mechanical pulp;
- Halted thermal reversion properties of hexadienol system;
- Studied the rates of ascorbic-acid catalyzed thermal reversion of high-yield pulps.

Design of Novel Photostabilization Reagents for Mechanical Pulp

Introduction

Research efforts over the past 45 years have identified three general methods by which mechanical pulps can be photo-stabilized. High-yield pulps can be stabilized by removing the lignin chromophores with a reducing agent followed by an alkylation procedure. This two-step process removes most lignin chromophores and stabilizes the pulp with respect to photoxidation of phenolic groups.[2] Alternatively, mechanical pulps can be stabilized by the addition of near-UV absorbing compounds such as dihydroxy or tetrahydroxy-benzophenone.[3] These latter reagents absorb harmful near-UV light and convert it to thermal energy thereby halting the photo-initiated oxidation of lignin. Although both of these processes are effective, the costs associated with these technologies have to date prevented their implementation.

The third alternative utilizes radical scavenging reagents which interrupt the oxidative reactions which ultimately cause brightness reversion. Early research efforts of Janson and Forsskahl demonstrated the efficiency of several mercaptans in retarding brightness reversion of high-yield pulps.[4] These observations have been further pursued by Sarkanen[5] and Daneault[6]. The results of their studies demonstrated that reagents such as thiogylcerol and 1-dodecanethiol can substantially improve the photo-stability of mechanical pulps. The use of ascorbic acid as an inhibitor of light reversion has also been explored. The effectiveness of this reagent and the proposed mechanism of photo-stabilization has been investigated by Heitner and others.[7]

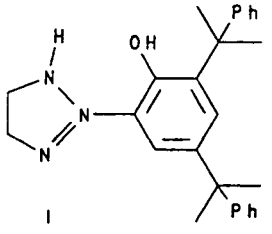
Based in part on the success of our previous screening studies we have continued to examine alternative reagents for photo-stabilizing mechanical pulps. The focus of this years screening activities have been directed towards the use of trialkyl phosphites, substituted triazoles, β-diketones, and mercapto-compounds. The first three classes of compounds have not been generally examined for photo-stabilizing high-brightness mechanical pulps but are frequently employed to protect synthetic polymers from photo and/or thermal degradation. The application of mercapto-compounds to photo-stabilize TMP and CTMP pulps has seen increasing attention and we have examined the use of novel sulfur compounds for high-brightness BCTMP pulps.

Results and Discussion

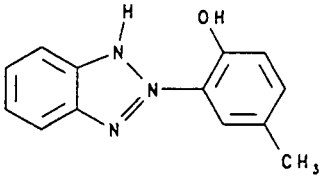
The photo-stabilizing effects of the additives were initially assessed employing the procedure developed in 1991. This procedure saturates a series of mechanical pulp handsheets with either a methanol/additive or methylene chloride/additive solution. After drying, the treated handsheets are irradiated with a xenon-arc lamp in the presence of non-treated handsheets. The relative rates of brightness reversion are then expressed in terms of % stabilization as described below:

% Stabilization = 100 * [(Δ Brightness of treated sample - Δ Brightness of reference sample)/Δ Brightness of reference sample)].

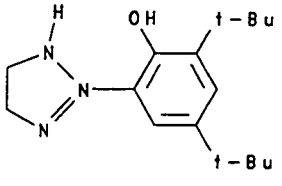
Our initial research activities were focused on studying the % stabilization effects of alkyl phosphites and substituted benzotriazoles. Alkyl phosphites have been shown to act as radical scavengers during accelerated aging studies for synthetic polymers. Furthermore, previous studies by McDonough et. al.[8] have shown that trimethyl phosphite readily bleaches mechanical pulps. These properties and their commercial acceptance suggested that they may have a potential application for mechanical pulps. Substituted triazoles are another class of compounds frequently employed for photo-stabilizing man-made polymers as these structures can efficiently absorb near-UV light. The structures examined in this year's studies are summarized below:



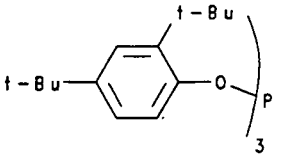
I



II



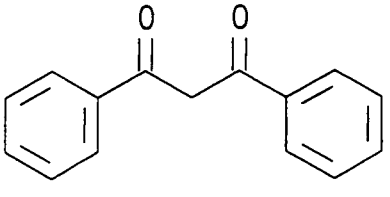
III



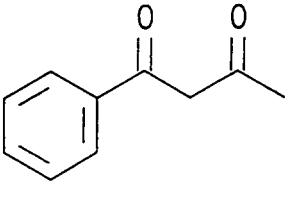
IV

The results of our photolysis experiments are summarized in Tables 1 and 2 and these data indicates that compounds I to III provided moderate reductions in the rates of brightness reversion for either softwood or hardwood BCTMP pulps. In contrast, the phosphite additive (IV) actually accelerated the photo-yellowing tendencies for both hardwood and softwood BCTMP pulps.

Accelerated photoaging studies with 1,3-β-diketones were found to be more promising. The two compounds studied were dibenzoylmethane (V) and 4-phenylbuta-2,4-dione (VI). Both of these compounds have been employed to stabilize man-made polymers and by extension we had anticipated that they may retard brightness reversion of mechanical pulps. Following our routine impregnation procedures, dibenzoylmethane (V) and 4-phenylbuta-2,4-dione (VI) were applied onto hardwood and softwood BCTMP test pads.



V



VI

As summarized in Table 3, compound VI provided substantial stabilization of both hardwood and softwood BCTMP handsheets. In comparison, additive V failed to provide even modest stabilization of either hardwood or softwood BCTMP handsheets. As significant as these results are, the data in general tend to suggest that the more hydrophobic a given additive is, the less effective it will be at stabilizing mechanical pulp. Differences in % stabilization of compounds V and VI were tentatively attributed to differences in the hydrophobicity of these two compounds. Comparable results were observed the previous year when we compared the % stabilization of 2,4-hexadien-1-ol (very effective stabilizer) versus 2,4-undecadien-1-ol (negligible stabilization).

In summary, these results support the hypothesis that efficient photo-stabilization of mechanical pulp requires that the additive exhibit excellent chemical and physical properties. It is presumed that the additive must maintain a proper balance of hydrophilic and hydrophobic interactions with the surface of the pulp fiber. The relatively poor % stabilization effects for the substituted triazoles have also been attributed to this hypothesis. Current research efforts in this area are therefore directed towards enhancing the hydrophobicity of triazole structure while maintaining their ability to absorb near-UV light.

The fundamental chemical mechanisms by which mercaptan derivatives photo-stabilize mechanical pulp were initially investigated by impregnating BCTMP handsheets with 2,2'-thiodiethanol, 2,2'-dithiodiethanol, and 2,2'-oxydiethanethiol. These reagents were selected since they provide the opportunity to examine the photo-protection effects of a thio-ether, a disulfide, and a di-thiol derivative for high-brightness BCTMP pulps. It was also anticipated that differences in photostabilization effects for the three additives would be readily correlated to chemical structure. Finally, all three compounds yielded simple, first order ^{1}H NMR spectra which we had anticipated would simplify spectral characterization of product mixtures.

Hardwood and softwood BCTMP handsheets were impregnated with the mercapto-compounds following our standard procedure of saturating the handsheet with a 0.089 N methanolic solution of the additive and then air-drying the handsheet. Tappi brightness readings taken before and after impregnation are summarized in Tables 4 and 5. These data indicate that only 2,2'-oxydiethanethiol bleached the BCTMP test sheets. Interestingly, the brightness bleaching gains were similar for the hardwood and softwood BCTMP handsheets. These results are consistent with Cole and Sarkanen's[5] previous results employing peroxide-bleached chemimechanical pulp despite the higher initial brightness values for the BCTMP pulps.

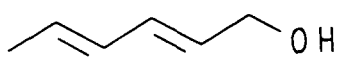
The results of our accelerated brightness reversion studies for the mercapto-impregnated softwood and hardwood BCTMP handsheets are summarized in Tables 6 and 7. A comparison of these results indicates that the di-thiol additive, 2,2'-oxydiethanethiol was the most effective reagent for retarding brightness reversion for softwood and hardwood BCTMP pulps. The second most effective reagent was 2,2'-dithiodiethanol

yielding % stabilization effects of approximately half the magnitude of the di-thiol compound. The relatively comparable % stabilization effects for both the softwood and hardwood pulp samples was of interest given the differences in lignin content and structure between softwood and hardwood BCTMP. Finally, 2,2'-thiodiethanol was the least effective photostabilization reagent for both BCTMP pulps studied.

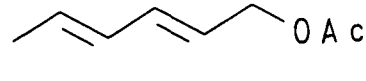
Although the photo-stabilization effects of thio-alkyl derivatives has been reported previously, our results demonstrate that 2,2'-dithiodiethanol can provide moderate photoprotection effects for the BCTMP pulps employed in this study. These results differ from previous studies[5] which had indicated that the disulfide functional group was of no value for stabilizing mechanical pulps for brightness reversion with CTMP or TMP pulps.

In light of continued interest in mercapto-stabilizers for mechanical pulp we have also examined their long term thermal reversion properties since potential future commercial applications will require that these additives exhibit thermal stability over extended periods of time. Figures 1 and 2 summarize the long thermal reversion properties for mercapto-additives impregnated onto softwood and hardwood BCTMP. These data indicate that the sulfur additives do not accelerate thermal reversion properties of BCTMP pulp and may even moderately retard this process.

Finally, we have also been successful in halting the accelerated thermal reversion tendencies of 2,4-hexadien-1-ol (VII) impregnated BCTMP handsheets. As reported in the previous PAC report, this additive exhibited significant photo-stabilization of mechanical pulps but apparently accelerated long term thermal reversion properties of high-yield pulps. We have now demonstrated that simple chemical modification of 2,4-hexadien-1-ol to the corresponding acetate (VIII, see below) halts the accelerated thermal reversion phenomena while maintaining its photostabilizing effects.



VII



VIII

Conclusions

The results of these survey studies have validated the application of thiol and disulfide structures for retarding brightness reversion of high-brightness mechanical pulps. Furthermore, we have identified β-diketones and triazoles as potential stabilizers of mechanical pulp provided that their affinity for the surface of pulp fibers can be enhanced. The potential application of diene-type structures in mechanical pulp has been further advanced since reversion issues have been mitigated.

Future Activity

Future research efforts will focus on optimizing the photo-stabilization effects of benzotriazoles, β-diketones, and mercapto-compounds. As these studies advance we will investigate potential synergistic effects of impregnating several additives onto mechanical pulp handsheets. Research efforts will also be directed towards incorporating these additive into a polymer based structure to further enhance their performance and prevent the loss of volatile, low molecular weight compounds. The effectiveness of these reagents will be assessed with conventional lighting sources as well as the solar simulator.

Fundamental studies of the mechanisms by which diene-type structures contribute to brightness stability are also under active investigation. Funding for these studies has been secured from a national competitive grant administered by USDA.

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Table 1 Brightness Stabilization Effects for Benzo-Triazoles I, II and III and Tris(2,4-di-t-butylbenzene)Phosphite (IV) Impregnated[a] Softwood BCTMP Sheets[b]

	% Stabilization Period of Irradiation/h		
	1	2	4
Additive			
I	28	31	33
II	31	34	31
III	36	36	36
IV	-4	-4	-5

[a]handsheets were saturated with a 0.089 N additive/methylene chloride solution; [b]average initial Tappi brightness=78.5, +/-1.0.

Table 2 Brightness Stabilization Effects for Benzo-Triazoles I, II and III and Tris(2,4-di-t-butylbenzene)Phosphite (IV) Impregnated[a] Hardwood BCTMP Sheets[b]

	% Stabilization Period of Irradiation/h		
	1	2	4
Additive			
I	37	32	46
II	37	50	45
III	14	35	43
IV	-10	-12	-5

[a]handsheets were saturated with a 0.089 N additive/methylene chloride solution; [b]average initial Tappi brightness=85.5, +/-2.0.

Table 3 Brightness Stabilization Effects for β-Diketone Additives Impregnated[a] on Softwood and Hardwood BCTMP Sheets[b]

	% Stabilization Period of Irradiation/h		
	1	2	4
Additive/Pulp			
V/Hardwood	9	17	20
V/Softwood	-10	0	20
VI/Hardwood	45	58	58
VI/Softwood	45	37	34

[a,b]see Tables 1 and 2 for description of experimental details.

Table 4 Brightness Values for Softwood BCTMP Pulp Sheets Impregnated[a] with Mercapto-Additives

Mercapto-Additive	% Applied[b]	Initial	TAPPI Brightness Impregnated	Brightness Gain
2,2'-thiodiethanol	2.4	80.1	80.5	0.4
2,2'-dithiodiethanol	2.8	80.3	80.5	0.2
2,2'-oxydiethanethiol	1.7	79.9	80.9	1.0

[a]handsheets were saturated with a 0.089 N methanolic solution of the additive; [b]% additive= weight of the additive added to handsheet/weight of the handsheet.

Table 5 Brightness Values for Hardwood BCTMP Pulp Sheets Impregnated[a] with Mercapto-Additives

Mercapto-Additive	% Applied[b]	Initial	TAPPI Brightness Impregnated	Brightness Gain
2,2'-thiodiethanol	1.6	87.7	87.8	0.1
2,2'-dithiodiethanol	1.8	87.4	87.1	0.3
2,2'-oxydiethanethiol	1.5	87.6	88.6	1.0

[a]handsheets were saturated with a 0.089 N methanolic solution of the additive; [b]% additive= weight of the additive added to handsheet/weight of the handsheet.

Table 6 Brightness Stabilization Effects for Mercapto-Impregnated[a] Softwood BCTMP Pulp Sheets

	% Stabilization Period of Irradiation/h				
	1	2	4	6	12
Mercapto-Additive[b]					
2,2'-thiodiethanol	10.3	7.7	8.8	9.0	11.9
2,2'-dithiodiethanol	38.0	34.7	33.1	26.1	25.7
2,2'-oxydiethanethiol	63.1	61.3	49.7	53.2	35.1

[a]handsheets were saturated with a 0.089 N methanolic solution of the additive; [b]see Table 2 for % additive applied onto handsheet and initial brightness values.

Table 7 Brightness Stabilization Effects for Mercapto-Impregnated[a] Hardwood BCTMP Pulp Sheets

	% Stabilization Period of Irradiation/h				
	1	2	4	6	12
Mercapto-Additive[b]					
2,2'-thiodiethanol	25.0	15.7	13.6	11.2	8.7
2,2'-dithiodiethanol	43.2	34.6	30.1	25.4	26.8
2,2'-oxydiethanethiol	70.0	62.5	57.1	47.3	31.1

[a,b]see Table 4 for experimental details.

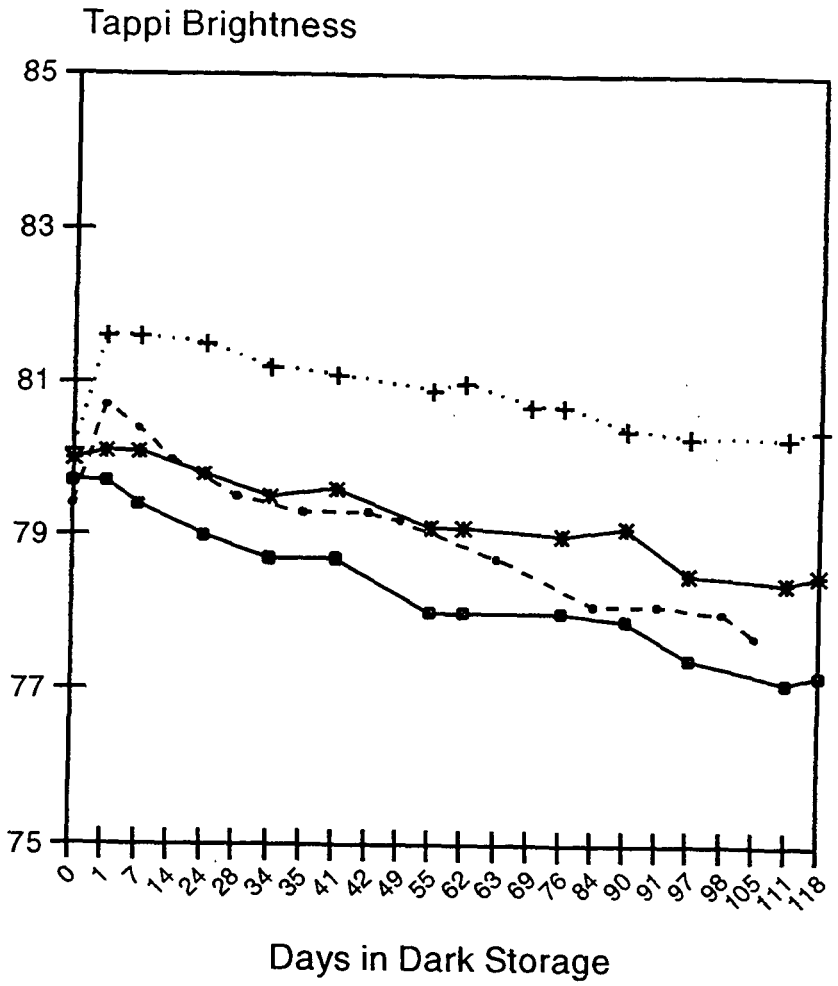


Figure 1: Long Term Thermal Reversion Properties of Mercaptan Impregnated Softwood BCTMP Handsheets

[a]% application is based on a wt/wt measurement

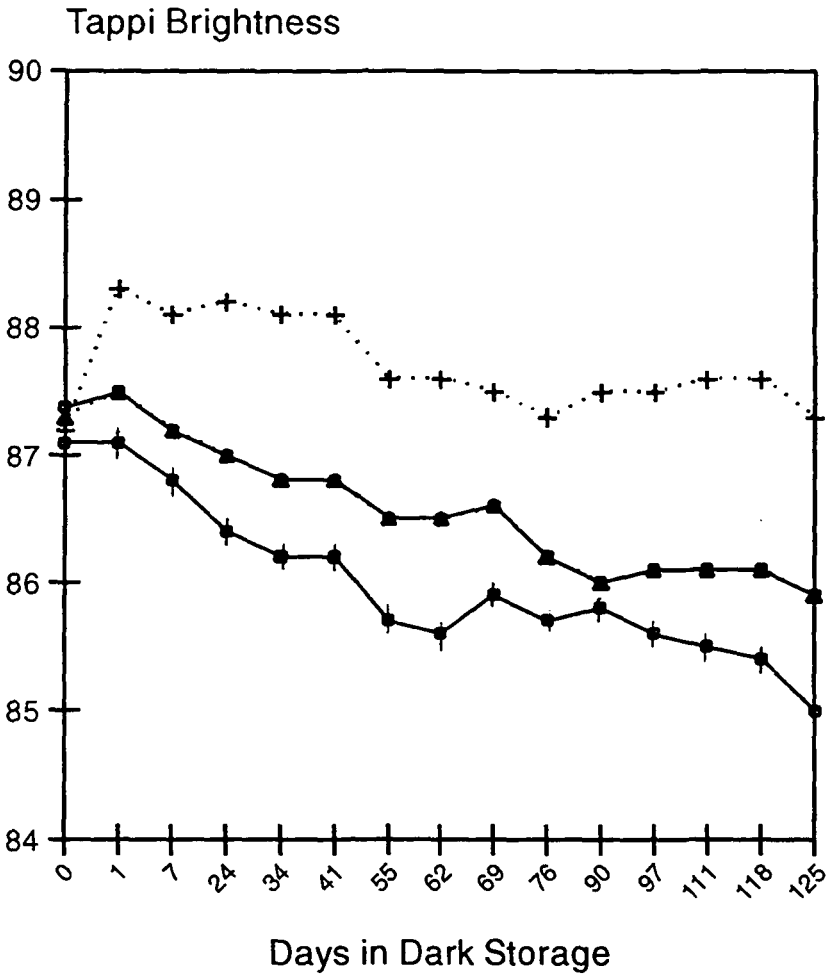


Figure 2: Long Term Thermal Reversion Properties of Mercaptan Impregnated Hardwood BCTMP Handsheets

[a]% application is based on a wt/wt measurement

Mechanistic Studies of Di-Mercapto Stabilizers for Mechanical Pulp

Introduction

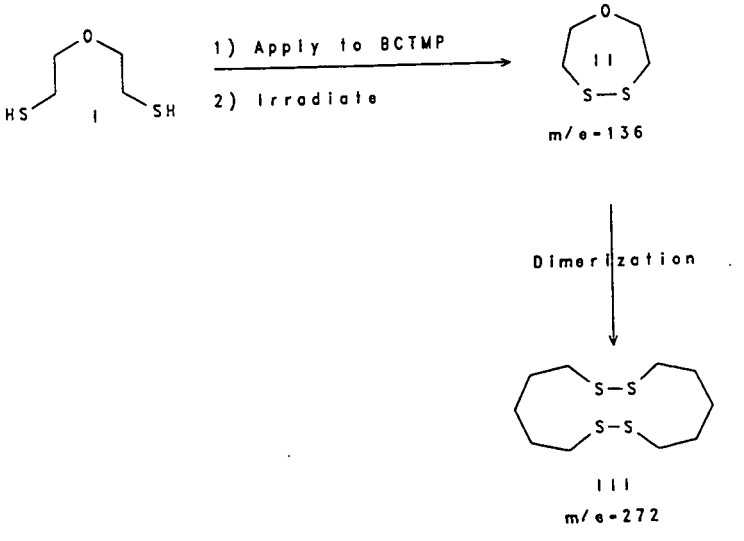
The continued development of photo-stabilizers for mechanical pulp will require an increased understanding of the mechanisms by which these additives interrupt the chemical pathways which contribute to brightness reversion. As part of our investigations we have initiated a detailed study of the chemical mechanisms by which dithio-ethers retard brightness reversion of mechanical pulp. The potential application of sulfur-containing compounds as brightness stabilization reagents for mechanical pulp was initially studied in great detail by Cole and Sarkanen.[1] These authors suggested that mercaptan stabilizers retard brightness reversion by a hydrogen donation mechanism thereby preventing the formation of phenoxy radicals and subsequent quinone formation. They also postulated that thio-stabilizers could undergo Michael-type additions to α-β-unsaturated systems thereby removing chromophoric compounds in the paper. Castellan[2] has supported this proposal suggesting that the primary photostabilization mechanism of mercaptan compounds is the reduction of photodegradation products and scavenging of prodegradent species such as hydroperoxides. These investigators also suggested that the molecular mobility of the stabilizers was an important component to their overall stabilization properties. In contrast, Daneault et. al.[3] proposed for the thio-reagents they studied that physical processes, such as molecular size occlusion was as important as chemical pathways for retarding color reversion.

Results and Discussion

To aid in designing new, more efficient mercapto-stabilizers and to advance the current state-of-the art knowledge of how these additives retard the photoyellowing process, we have examined the chemical reactivity of 2,2'-oxydiethanethiol during brightness reversion. The general methodology we employed for these studies was to impregnate a series of cellulose and hardwood BCTMP handsheets with 2,2'-oxydiethanethiol (I), irradiate the handsheets with a xenon-arc lamp, extract, and characterize the oxidized products.

Following our general impregnation procedure, hardwood BCTMP handsheets were saturated with a 0.089 N methanolic solution of 2,2'-oxydiethanethiol followed by air drying and irradiation for 2 and 12 h on each side of the handsheet. After photolysis, the handsheets were shredded and continuously extracted for 14 h with methylene chloride. The methylene chloride extracts were then concentrated and examined by GC/MS and ^{1}H NMR. The proton 1-D and 2-D COSY NMR of the methylene chloride extracts for the 2 h photolysis experiment are shown in Figure 1. The predominant signals centered at δ3.62, 2.71, and 1.62 ppm can be readily attributed to the starting material. The apparent lack of signals in the δ6.6-8.0 ppm range clearly indicates that the extraction process does not remove lignin-like structures from the irradiated pulp samples. The COSY spectrum clearly indicates that the triplets at δ4.06/2.95 and 3.74/2.91 are coupled to each other. The differences in peak intensities for these two sets of signals and the lack

of cross peaks between these sets of signals suggested that two new products had been formed during photolysis. Furthermore, the apparent similarities in coupling patterns suggested that these new products had been formed from 2,2'-oxydiethanethiol. GC/MS analysis of the extracts indicated the presence of starting material and two new major components with m/e of 136 and 272. The two new components were readily attributed to 1,4-oxadithiane (II), the oxidized cyclic form of 2,2'-oxydiethanethiol and the second component was attributed to the dimer of III. These structures are presumably formed by means of an oxidative cyclization process, as summarized below:

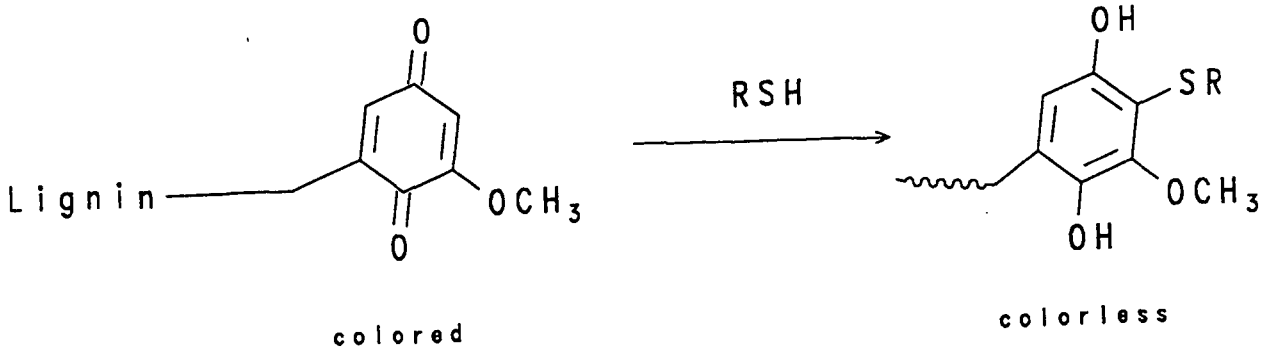


The oxidative cyclization of dithiols is well known in the literature[4] and it has been demonstrated that the all carbon analogue of 2,2'-oxydiethanethiol (i.e. 1,5-dithiolpentane) can be readily cyclized.[5] Dimerization of cyclic disulfides has also been shown to occur under a variety of reaction conditions and we remain uncertain as to what extent the dimer is formed during photolysis and/or during the extraction procedure.

Although the presence of II in the methylene chloride extracts suggested that di-thiol I retards brightness reversion by undergoing an oxidative cyclization reaction the well known propensity of di-thiol compounds to undergo autoxidation reactions made this conclusion tenuous. Control experiments established that the simple impregnation/extraction procedure did yield minor amounts of II and III. The presence of II and III after impregnation and extraction was attributed to the bleaching reactions which occur during impregnation. Photolysis of cotton linter handsheets impregnated with I also yielded trace amounts of I although the amounts were significantly less than that generated by photolysis on hardwood BCTMP handsheets. In summary, although the experimental procedures employed in these experiments yielded trace amounts of II and III, their formation is dramatically increased when the accelerated photo-aging studies are

preformed on BCTMP handsheets. These results clearly demonstrate that the thiol derivatives function in-part as a source of hydrogen during brightness reversion conditions.

Although these research efforts were able to identify contributing mechanisms of stabilization, our analyses were dependent upon isolating the oxidized additive. Clearly, this approach precluded studying any chemical process which would permanently link the additive to the lignin in the pulp. These types of reactions, as shown below have been speculated to contribute to the photo-stabilization effect although no experimental data substantiating this process has been acquired.



To investigate the potential incorporation of the additive to the lignin in pulp, we impregnated a series cotton linter and hardwood BCTMP handsheets with 2,2'-oxydiethanethiol and irradiated the handsheets for 12 hours. After photolysis the handsheets were extracted and analyzed for sulfur. Elemental analysis indicated that simple impregnation and extraction of cellulose or mechanical pulp handsheets removed all detectable sulfur. Irradiation and extraction of the di-thiol/cotton linter handsheets also removed all traces of sulfur from the handsheet. In contrast, extraction of the irradiated di-thiol/BCTMP handsheets did not remove all of the sulfur additive. After 12 h of irradiation the extracted handsheets contained 1.3% sulfur (by weight). Repeating the photolysis experiment for 24 h followed by methylene chloride extraction yielded handsheets containing 1.5% sulfur. The presence of unextractable residual sulfur in irradiated BCTMP handsheets has been attributed to the formation of a chemical bond between lignin structures and the thiol additive.

Conclusions

In summary, we believe that we have experimentally established the dominant mechanisms by which thiol derivatives photo-stabilize mechanical pulp. The results of our studies indicate that thiol additives may retard brightness reversion by potentially interrupting oxidative pathways and by addition into conjugated lignin structures. The

relative importance of each of these mechanisms remains unclear and will require further investigation. Nonetheless, our current results suggest that future sulfur based additives will need an optimal balance of oxidative properties and nucleophilicity to retard the overall photo-yellowing process.

Future Research Activity

Future studies in this area will focus on applying these results towards increasing the photo-stabilization effects of thiol based additives. Furthermore, research efforts will be directed towards incorporating these thiol compounds into a polymeric formulation. The use of a polymer based additive has several advantages but we believe one of the principal returns will be the development of a non-odorous thiol additive which will retain most of the benefits of the monomeric structure.

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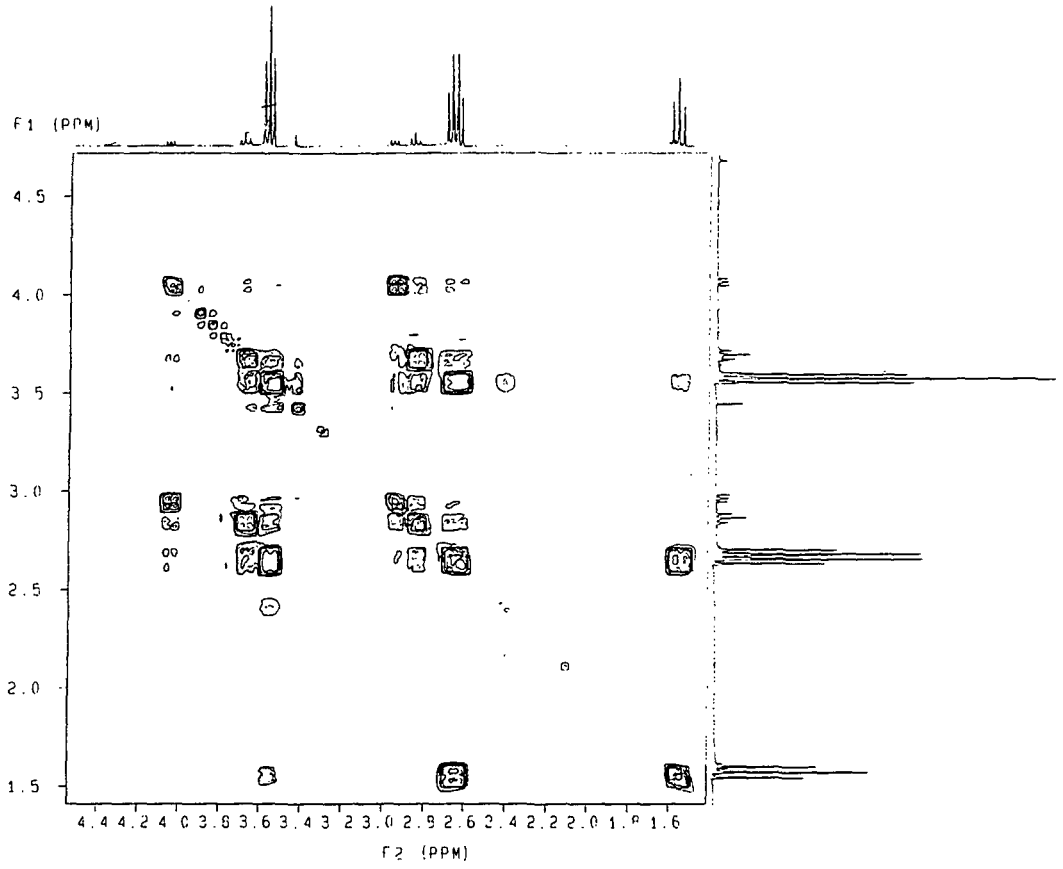


Figure 1: 1-D ^{1}H NMR and COSY Data for Methylene Chloride Extracts from the 2 h Photolysis of 2,2'-oxydiethanethiol/Hardwood BCTMP Handsheets.

Thermal Aging of Ascorbic Acid Impregnated Lignin-Retaining Pulps

Introduction

The efficacy and generally recognized safety of ascorbic acid as a chemical preservative has lead to an increased interest in the application of this reagent to photo-stabilization of mechanical pulps.[1] The successful incorporation of this reagent into mechanical pulps will require that the additive exhibit several important properties including; outstanding light stabilizing abilities, cost-effectiveness, no color contribution, and excellent long term thermal aging properties. Although ascorbic acid fulfills many of these requirements it is well known that the autoxidation tendencies of this reagent have limited several commercial applications. This report presents our initial studies directed at examining the thermal aging properties of ascorbic acid impregnated BCTMP test handsheets.

Results and Discussion

To establish the outcome of long term thermal aging on ascorbic acid impregnated mechanical paper we saturated a series of BCTMP testsheets with a 0.02 N methanolic ascorbic acid solution. After drying under vacuum the handsheets were weighed and stored in the dark at -10°C. The impregnation procedure applied an average of 1.5% (wt/wt) ascorbic acid onto BCTMP handsheets.

The photo-yellowing tendencies of these impregnated handsheets were assessed by irradiating impregnated handsheets with a xenon-arc lamp. All irradiations were performed in triplicate, in the presence of three untreated handsheets. Analysis of the photo-yellowing properties of ascorbic acid treated BCTMP handsheets and untreated handsheets indicated that treated handsheets exhibited % stabilization effects of ca 60% during the four hours of irradiation. These results are consistent with previously reported literature results[1] and demonstrates the effectiveness of ascorbic acid at retarding overall rates of brightness reversion and validates our impregnation procedures.

Obviously for commercial applications it is necessary that the stabilization effects are not significantly diminished by lengthy periods of storage. To investigate the thermal stability of ascorbic acid impregnated handsheets we had initially planned to store treated handsheets in a constant temperature and relative humidity room for three months and then repeat the accelerated photo-aging studies. These experiments were precluded when it was observed that treated hardwood BCTMP handsheets underwent relatively rapid thermal discoloration upon standing in the dark for 40 days. Brightness analysis of hardwood BCTMP handsheets impregnated with 2% ascorbic acid indicated that the handsheets lost 8% of their initial brightness values. In comparison untreated handsheets had lost only 1% of their initial brightness value over the same time period. Clearly, this previously unreported thermal discoloration of ascorbic acid impregnated handsheets could significantly impact any future commercial considerations of this reagent with

mechanical pulp. To determine the magnitude of the thermal reversion properties for vitamin C impregnated BCTMP pulps we initiated a series of long term thermal aging experiments. The results of these studies and our initial attempts to develop a co-additive to retard the thermal reversion properties for ascorbic acid impregnated BCTMP testsheets are summarized in this report.

The rates of thermal reversion for ascorbic acid impregnated BCTMP handsheets were monitored against the thermal reversion tendency of non-treated, methanol extracted BCTMP brightness pads. The results of the thermal aging studies for softwood and hardwood BCTMP and cellulose test pads are summarized in Figure 1. The thermal reversion data shows that ascorbic acid treated mechanical pulp samples exhibit an initial brightness gain after impregnation with vitamin C. This initial gain in brightness has been previously noted by Robinson et. al.[2] and is attributed to a reductive bleaching effect of vitamin C. Despite this gain in brightness the samples rapidly undergo thermal reversion and within approximately 20 days, the treated handsheets have returned to their initial brightness values. The treated test sheets continue to darken in a near linear manner for the next 100 days resulting in the loss of 14 brightness points for the hardwood BCTMP handsheets and 11 brightness points for the softwood BCTMP handsheets. In contrast, the untreated sheets exhibit a minor drop in brightness of ca 2 1/2 brightness units for the softwood and hardwood BCTMP pulp samples.

As summarized in Figure 2 the ascorbic acid/cellulose handsheets also exhibited moderate thermal reversion tendencies. A comparison of these results with those observed for the BCTMP pulps containing ascorbic acid indicates that the cellulose treated handsheets undergo thermal reversion at a slower rate. Although we remain uncertain as to the exact nature of the mechanisms contributing to these differences in rates these results demonstrate that relative rates of thermal reversion are influenced by the nature of the test handsheet.

To explore potential methods of retarding the ascorbic acid accelerated thermal reversion of BCTMP we examined the use of methanolic solutions of polyethylene glycol and ascorbic acid. Minemura[3] and Forsskahl[4] have demonstrated that the application of polyethylene glycol onto mechanical pulp retards the overall rate of thermal reversion. Although the exact mechanism(s) contributing to the reduction in rates remains uncertain we had hypothesized that the use of ascorbic acid and polyethylene glycol could potentially yield a thermal and photostable mechanical pulp. To explore this hypothesis we employed two differing degrees of polymerization samples of polyethylene glycol with average molecular weights of 200 and 8000. The thermal reversion data for BCTMP test sheets impregnated with either polyethylene glycol/ascorbic acid or polyethylene glycol are summarized in Figures 3 and 4. A review of this data indicates that although the polyethylene glycol BCTMP treated samples reverted slower than the non-treated pulp samples the ascorbic acid/polyethylene glycol samples continued to exhibit significant thermal reversion properties.

Conclusions

The experimental data presented in this report indicates that thermal reversion properties of ascorbic acid impregnated BCTMP handsheets poses a serious challenge for any commercial applications. The results of these studies highlight the need to develop a co-additive which will retard thermal reversion and maintain the photo-protection effect of ascorbic acid. In a more general perspective, these results serve to emphasize the complex and demanding requirements placed upon any additive which is to be employed for photo-stabilizing mechanical pulps.

Future Research Activities

Future research efforts will focus on the continued examination of alternative co-additives for ascorbic acid which may enhance its long term thermal and photo-stabilizing effects.

References

1. Heitner, C.; Schmidt J.A. 6th International Symposium on Wood and Bleaching Chemistry, TAPPI Proc., TAPPI Press, Atlanta, 131(1991).

2. Robinson, J.C.; Grimsley, S.A.; Jeffery, D.J.; Schroeder, M.A., Tappi Pulping Conference, 167(1988).

3. Minemura, N., Mokuzai Gakkaishi, *24*(8), 587(1978).

4. Janson, J.; Forsskahl, Nordic Pulp Paper Res. J., 197(1989).

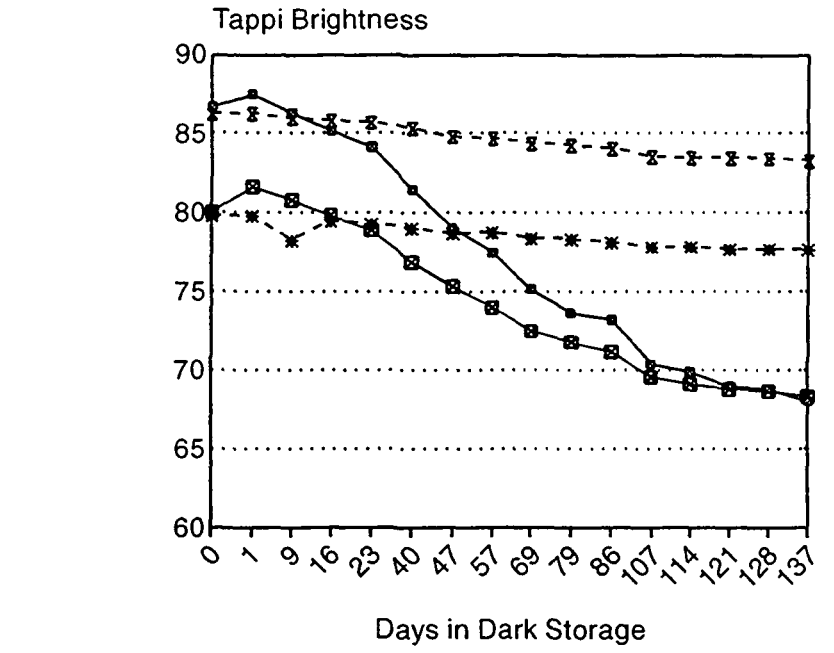


Figure 1: Long Term Thermal Reversion Properties of Ascorbic Acid Impregnated Softwood and Hardwood BCTMP Handsheets

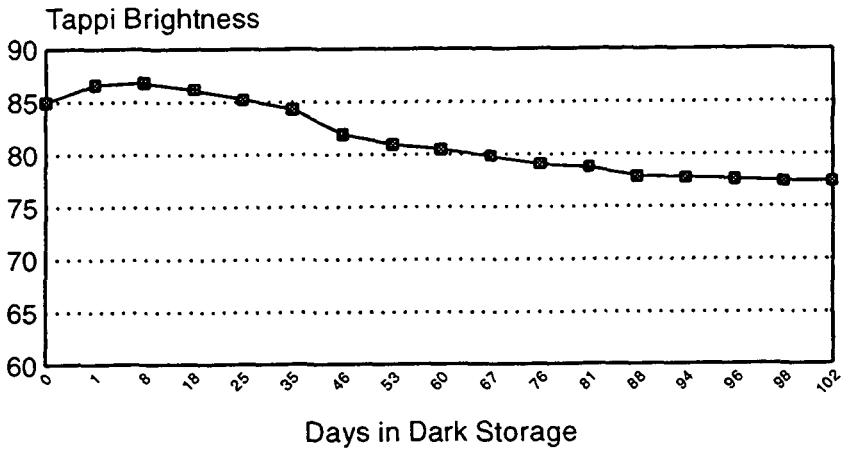
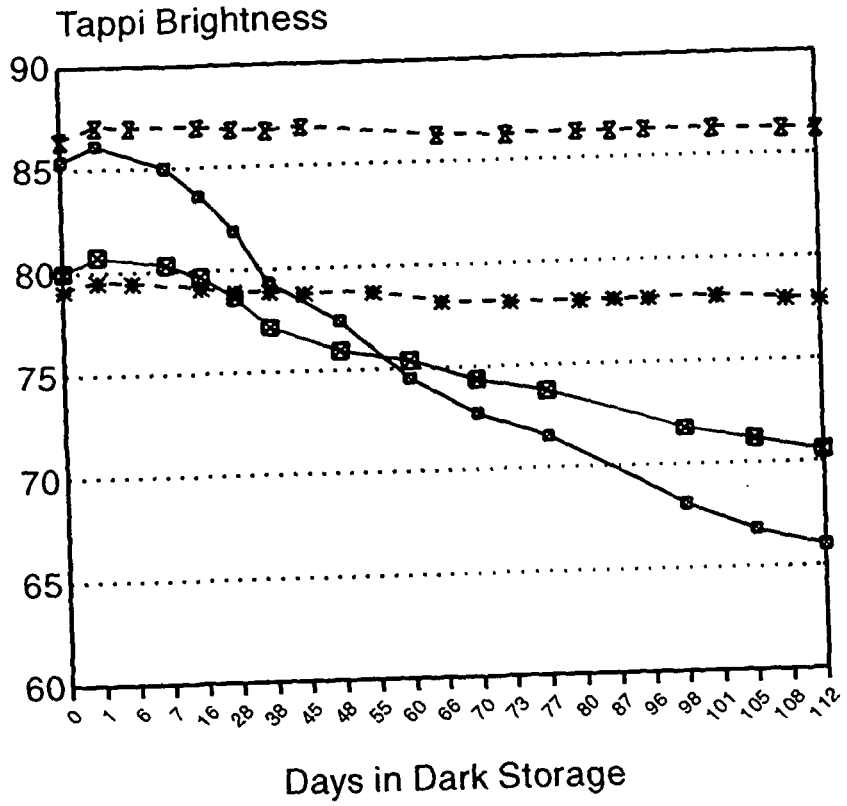


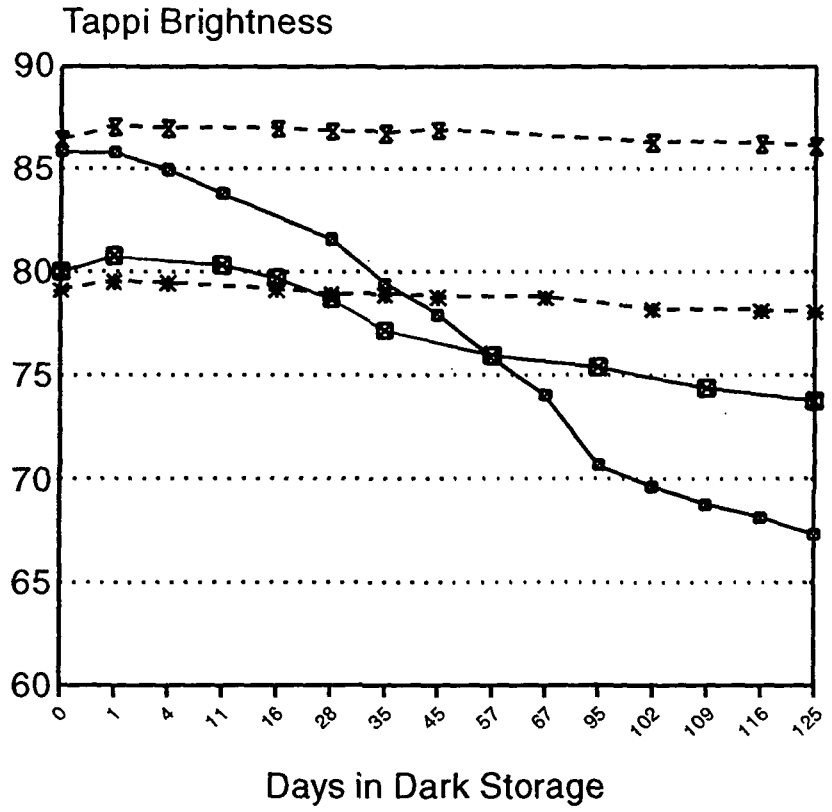
Figure 2: Long Term Thermal Reversion Properties of 1% Ascorbic Acid Impregnated Cellulose Handsheets(wt/wt).



- 1% Ascorbic Acid/Polyethylene Glycol (MW:200)/Softwood BCTMP[a]
- 1% Ascorbic Acid/Polyethylene Glycol (MW:200)/Hardwood BCTMP
- 1% Polyethylene Glycol (MW:200)/Softwood BCTMP
- 2% Polyethylene Glycol (MW:200)/Hardwood BCTMP

Figure 3: Long Term Thermal Reversion Properties of Ascorbic Acid Impregnated/Polyethylene Glycol (MW:200)/BCTMP Handsheets

[a]% application is based on weight of additives/wt of handsheet



- 1% Ascorbic Acid/Polyethylene Glycol (MW:8000)/Softwood[a]
- 2% Ascorbic Acid/Polyethylene Glycol (MW:8000)/Hardwood[a]
- 1% Polyethylene Glycol (MW:8000)/Softwood BCTMP[a]
- 1% Polyethylene Glycol (MW:8000)/Hardwood BCTMP[a]

Figure 4: Long Term Thermal Reversion Properties of Ascorbic Acid Impregnated/Polyethylene Glycol (MW:8000)/BCTMP Handsheets

[a]% application is based on weight of addiitives/wt of handsheet

ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED CHEMICAL PULP

PROJECT 3474

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ANNUAL RESEARCH REVIEW
APRIL 28, 1993

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
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TECHNICAL PROGRAM REVIEW REPORT

Date:	April 5, 1993
Project Title:	ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED CHEMICAL PULP
Project Staff:	T.J. McDonough, M. Carden, C.E. Courchene, T. Kubicar, H. Ham, T. Ard, T. Schwantes, C. Walker, C. Pupier
Budget (FY 92-93):	$634,000
Reporting Period:	March 1992 - March 1993
Project Number:	3474

OBJECTIVE:

Define pulping and bleaching technology that will decrease or eliminate the release of byproduct organic chlorine compounds without sacrificing bleached pulp quality.

GOALS:

A. Totally Chlorine-Free Bleaching

1. Identify residual lignin structural features likely to be of importance in defining bleachability.

2. Assess the role of carboxyl group introduction in the mechanism by which chemical pretreatments improve the selectivity of a subsequent oxygen delignification stage.

3. Define effects of phenolic hydroxyl groups, alpha carbonyl groups and other lignin structural features on ease of lignin removal by oxygen, ozone and hydrogen peroxide, in comparison with the corresponding effects on ease of lignin removal by chlorine and chlorine dioxide.

4. Assess the importance of lignin-carbohydrate bonds as a factor determining ease of lignin removal by oxygen and alkali, in comparison with the corresponding effects on ease of lignin removal by chlorine and chlorine dioxide.

5. Determine the rate law governing the kinetics of cellulose degradation by ozone.

6. Establish effects of delignification with kraft pulping liquor, oxygen and ozone on cellulose characteristics (viscosity, carboxyl content, etc.), pulp refining behavior and papermaking properties, and compare with corresponding effects of delignification with chlorine and chlorine dioxide.

7. Determine effects of degree of oxygen dispersion on medium consistency oxygen bleaching.

8. Establish experimental techniques for measuring selectivity of catalyzed hydrogen peroxide delignification in a model system.

9. Evaluate novel chlorine-free bleaching agents.

10. Compare toxicity of ozone bleaching effluents to that of effluents from bleaching with chlorine dioxide and chlorine.
(New goal; to be addressed within the academic research program.)

11. Evaluate sulfite-anthraquinone-nonchlorine routes to high- brightness, kraftlike pulps.
(New goal; to be addressed within the academic research program.)

B. Environmentally Compatible Bleaching with Chlorine Compounds

1. Quantify the effect of mixing on AOX and chlorophenols formation over a wide range of kappa factors in CE, (CD)E and DE partial bleach sequences.

2. Develop techniques for characterizing the AOX in (DC)E_{OP} and DE_{OP} partial bleach sequences.

3. Compare toxicity of effluents from chlorine dioxide delignification with that of effluents from delignification with chlorine and ozone. (New goal; to be addressed within the academic research program.)

SUMMARY:

Research has included investigations of chlorine compound free systems on one hand and chlorine and chlorine dioxide based ones on the other.

Totally Chlorine-Free Bleaching

Effects of residual lignin structure on bleachability comprise the focus of one set of project goals (Goals A1-A4). An earlier study showed that acid groups contribute only

modestly to the ease of lignin removal by oxygen and alkali, and therefore to its selectivity. In a second study, the ease of carbohydrate removal from pretreated pulp samples by a cellulolytic enzyme was found not to correlate with bleachability, perhaps as a result of the unexpectedly high lignin solubility in the enzyme solution. The effect of xylanase pretreatment on oxygen bleachability was also assessed, as an indicator of the importance of lignin-carbohydrate bonds. A modest improvement was observed.

During the current period, the level of effort expended in this area has been limited by availability of personnel. Staff addition is expected in April, 1993 to remedy this situation.

The kinetics of ozone depolymerization of cellulose has been studied in a stirred semibatch flow reactor using cotton linters as the principal substrate. Earlier results showed that the process exhibits two distinct rate phases. The initial phase is rapid and has a rate that depends on both the ozone concentration and the extent of depolymerization; the second phase is slower and depends only on ozone concentration, showing no tendency to slow down with increasing extent of depolymerization. The rapid phase, complete in just a few minutes, may account for a substantial fraction of the total viscosity loss during ozone bleaching.

More recently, a redesign of the experimental system was carried out to simplify data acquisition and improve flow control. It has also been necessary to devote considerable effort to overcoming problems with fines interference in ozone detection and with clumping of the cotton linters. Runs have been carried out to confirm the dependence of the reaction rate on consistency and to determine the persistence of zero-order kinetics (constancy of reaction rate) at long reaction times. Current work is aimed at establishing the effects of ozone concentration on the reaction rates and rapid phase duration.

Processes for delignification with oxygen suffer from an incomplete knowledge of **dispersion of oxygen into medium consistency pulp**. Our approach to this problem involves establishing the relationship between gas-liquid interfacial mass transfer and the operating parameters of a laboratory-scale, semicontinuous, fluidizing mixer. The method consists of determining the amount of carbon dioxide absorbed by an alkaline medium consistency pulp suspension under systematically varied conditions of mixer operation. Earlier work resulted in the establishment of methods and preliminary relationships between interfacial area developed and operating conditions.

A search for ways to mimic the action of enzymes in **catalyzing hydrogen peroxide delignification** is the subject of a current Ph.D. thesis (Ms. C. Walker). A lignosulfonate and hydroxyethylcellulose are being used as soluble polymeric models for lignin and cellulose, respectively. High pressure size exclusion liquid chromatography and solution viscosity are being used to determine extent of degradation of the models, and concentrations of hydroxyl radicals are being determined by a chemiluminescence method. Methods development for all three procedures was the subject of earlier work on this thesis.

A joint effort with the Wood Chemistry Group has focussed on the potential of dimethyldioxirane (DMD, a cyclic peroxide) as a **novel delignifying agent**. DMD was generated in situ from peroxymonosulfuric acid and acetone and shown to be capable of extensively delignifying kraft pulp.

The Ph.D. thesis of research of Ms. T. Ard will examine the **toxicity of ozone bleaching effluents** in comparison of those from chlorine dioxide delignification and the more classical chlorination stage.

Environmentally Compatible Bleaching with Chlorine Compounds

At low kappa factors, very good **mixing during chlorination** sharply reduced the rate of AOX generation. This effect was even more apparent when it was evaluated at fixed CE kappa number rather than at fixed kappa factor, because of the effect of mixing on delignification. At a CE kappa number of 7, the effluent AOX reduction attributable to improved mixing was approximately 60%.

A Ph.D. thesis research project by T. Schwantes is aimed at the **characterization of the chlorinated organic compounds formed during bleaching** and to determine effects of bleaching process changes on their characteristics. Analysis of a chlorination effluent has shown that about half of its nonvolatile material was ether extractable and that the chlorine-to-carbon ratio was much higher in the ether extractable than in the nonextractable fraction. About 85% of the extractable fraction was acidic, 9% was phenolic and 6% neutral. For the extraction effluent analyzed, 60% of the nonvolatile material was ether extractable. Of this, 83% was acidic, less than 2% was phenolic, and 15% was neutral.

The Ph.D. thesis research of Ms. Teri Ard will examine the **toxicities of chlorine dioxide delignification effluents** in comparison with those from chlorination and ozone bleaching.

RECENT RESULTS

Ozone Kinetics

Experiments were done with the apparatus essentially as shown in Figure 1. Ozone was predissolved in buffer solution (0.4M acetic acid/0.0072M sodium acetate, pH 3) and the solution then flowed, at constant rate and concentration, to the reactor vessel. The effluent stream from the reactor vessel was analyzed by ultra-violet spectroscopy for ozone. After steady state was established a sample of cotton linters was added to the reactor. The linters sample was prevented from leaving the reactor by a fine mesh plastic screen at its outlet.

In the experiments reported earlier, the expected drop in the reactor effluent ozone concentration was observed upon addition of the linters sample. This was due to consumption of ozone by the added sample. When experiments were resumed with a different linters sample, however, an apparent increase in effluent ozone concentration was observed when the linters sample was added. This was shown to be due to fines being washed from the sample into the reactor effluent. The fines scattered the spectrometer beam leading to an increase in apparent absorbance and appearing as an increase in the ozone concentration. This can be seen in the first two runs shown in Table 1 as an apparent negative rate of ozone disappearance. Washing the linters on a large mesh screen prior to the run failed to cure this problem, as shown by the data for run 3 in Table 1. Prefractionation of the linters by Bauer-McNett classification was then tried, with mixed results, as shown for runs 4 through 13. The poor reproducibility of these runs may be due to a combination of incomplete fines removal and metal ion contamination occurring during the Bauer-McNett procedure.

To evaluate the contribution of incomplete fines removal to the variability in the above data, fines-free samples were prepared by using the reactor itself as a screening device. In a typical experiment, the reactor was set up in a steady state flow condition, but with no ozone being fed to the system. The UV absorbance of the effluent was monitored, as a measure of the rate of fines release. Figure 2 is a UV trace from such an experiment, showing that appreciable fines release occurs for about 15 minutes. Figure 2 indicates that the effect of fines release on initial slope measurements is difficult to predict. The slope of Figure 2 varies from a large positive value to a large negative value within a very short time period following linters addition. The maximum absorbance in Figure 2 is only about 15% of the absorbance due to ozone in a typical experiment, but this is less relevant than the slope for initial rate measurements.

The remaining runs shown in Table 1 were done under various conditions of prefractionation of the linters and probably also with various degrees of success in avoiding contamination of the linters with metals. During the course of these runs, several other changes were made, including addition of online ozone measurement and data acquisition capability. Another change made during this time period was the introduction of PFI milling of the linters before using, to shorten the fibers and reduce their tendency to clump and wind around the impeller shaft.

FIGURE 1

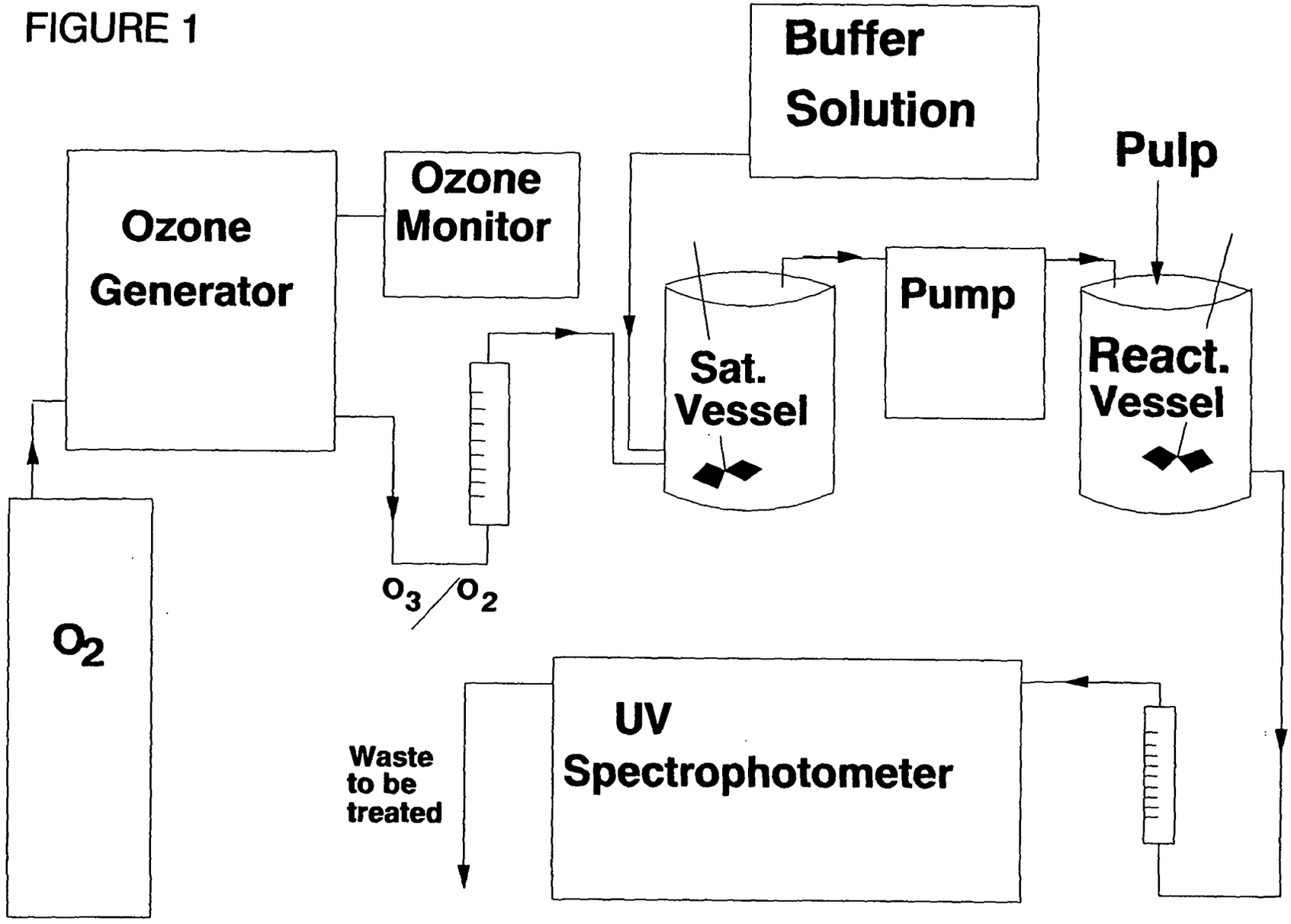

Buffer Solution
Pulp
Ozone Generator
Ozone Monitor
Pump
Sat. Vessel
React. Vessel
O_3 / O_2
O_2
Waste to be treated
UV Spectrophotometer

Table 1. Results of Preliminary Experiments on Ozone-Cotton Linters Kinetics

Run No.	Init. Ozone Conc., mg/L	Ozone Flow Rate, mL/min	Pulp Type	Consistency, %	Run Time, min	Init. Visc., cp	Final Visc., cp	$-dO_3/dt$, mg/L/min	Note
1	12.9	250	Linter A	0.2	2	274	nd	-28.9	1
2	12.2	250	"	0.3	3	"	68.8	-22.5	1
3	11.3	250	"	"	2	"	nd	-10.8	2
4	11.0	250	"	"	"	"	nd	-0.85	3
5	12.6	250	"	"	3	"	70.0	0.93	3
6	12.5	250	"	"	8	"	nd	0.24	3
7	9.1	250	"	"	20	"	"	-0.13	3
8	9.6	250	"	"	"	"	"	0.22	3
9	14.6	100	"	0.1	5	"	28.4	0.00	3
10	15.3	120	"	"	10	"	14.7	0.02	3
11	15.0	95	"	"	20	"	11.5	0.79	3
12	12.7	100	"	"	30	"	8.4	0.37	3
13	13.5	90	"	"	30	"	7.45	0.35	3
14	15.8	90	Linter B	"	30	51	7.94	1.28	4
15	14.1	90	"	"	30	"	8.13	1.08	4
16	13.7	90	"	0.3	5	"	19.8	0.62	4
17	12.7	87	"	"	10	"	12.3	0.20	4
18	16.1	110	Linter A	"	20	274	9.2	0.78	4
19	16.4	92	Linter B	"	30	51	5.74	0.13	5
20	17.1	90	"	"	"	"	5.52	0.31	4
21	15.8	90	"	"	"	"	7.54	1.62	4
22	14.1	86	"	"	"	"	9.25	1.29	4
23	5.62	90	"	0.2	"	"	9.43	-0.5	1
24	6.38	"	"	"	"	"	9.6	-0.08	1
25	7.86	"	"	"	"	"	11.12	0.04	6
26	7.03	"	"	"	"	"	10.88	0.022	6

Notes for Table 1

1. Apparent increase in ozone concentration upon pulp addition due to fines release.
2. Linters washed to remove fines prior to run.
3. Linters prefractionated on Bauer-McNett classifier to remove fines.

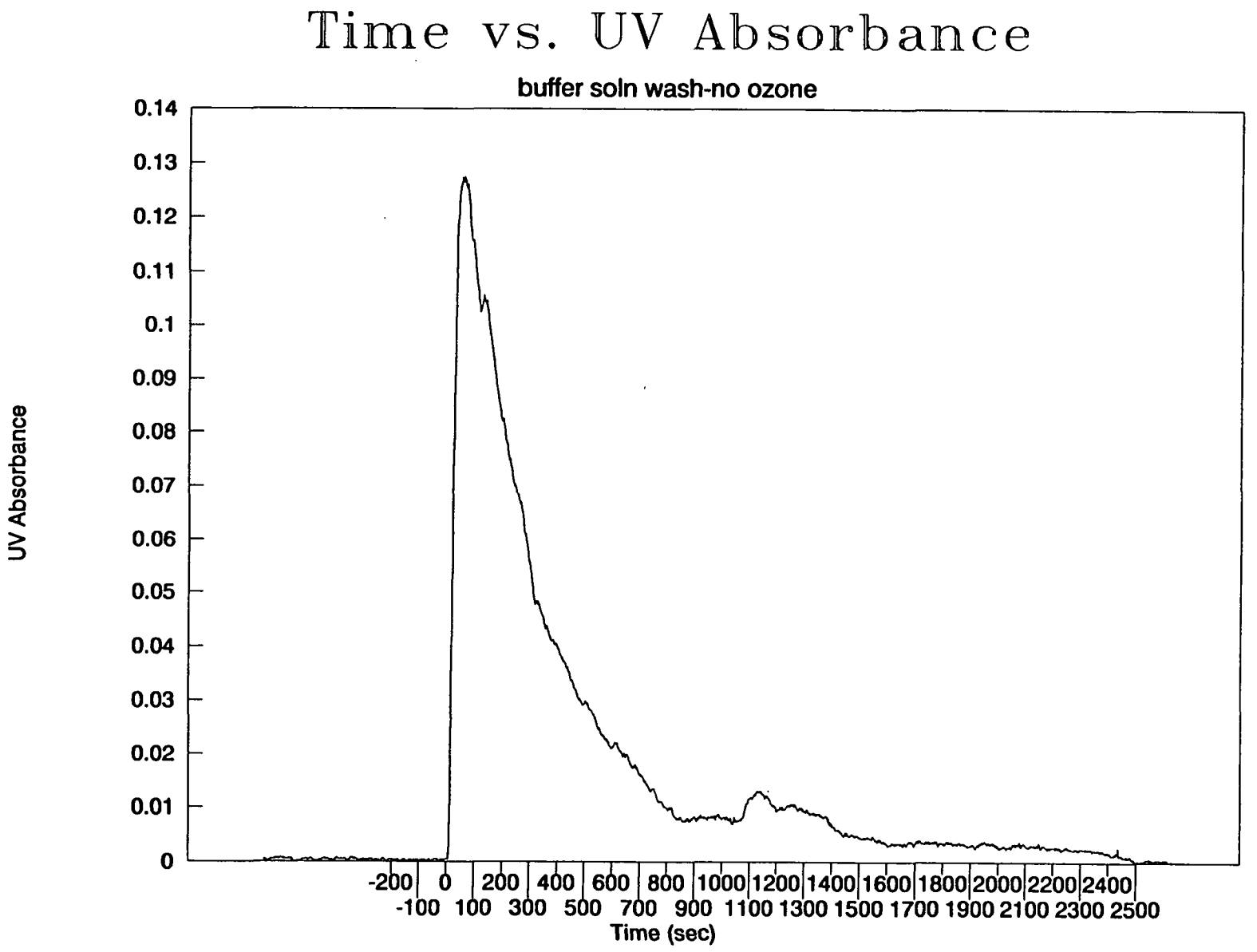

Time vs. UV Absorbance
buffer soln wash-no ozone
UV Absorbance
0.14
0.13
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
-200 0 200 400 600 800 1000 1200 1400 1600 1800 2000 2200 2400
-100 100 300 500 700 900 1100 1300 1500 1700 1900 2100 2300 2500
Time (sec)

FIGURE 2

4. Linters prefractionated in ozonation reactor to remove fines.
5. Linters not prefractionated.
6. Linters prefractionated on Sweco screen to remove fines.

Unfortunately, PFI milling created fines and placed additional demands on the fines removal procedure. The last two runs were done on linters prefractionated on a Sweco screen. This was shown to be an effective method of fines removal that did not require exposure to large volumes of water. Control experiments, such as the one that was earlier used to provide the data in Figure 2, confirmed that Sweco screening reduced fines content to very low levels. This procedure was therefore adopted for the remaining runs, shown in Table 2. The reproducibility of the initial rate data in Table 2 is much better than that of Table 1, indicating that our efforts to improve the apparatus and procedure have been successful.

The data in Table 2 must be considered in the light of the relationship between the reactor outlet concentration and the kinetics of the reaction. This relationship is given by the mass balance around the reactor:

$$\frac{dc}{dt}=\frac{c_o-c}{\tau}+r$$

At the very beginning of the reaction, just after the linters sample is added, $c=c_o$, the first term on the right hand side disappears, and the reaction rate is equal to dc/dt, the initial slope of the concentration profile. Thus, one way to approach the data is to concentrate only on this initial slope, and this is what has been done to date. A better way is to analyze the entire concentration-time profile in terms of the above mass balance equation, to obtain the relationship between r and c. This will be done, now that we have attained the required level of confidence in the quality of the data.

The first eight runs in Table 2 were done to determine the effect of consistency. The initial rate was observed to increase with increasing consistency, over the range 0.05 to 0.4%. If the rate equation is assumed to be of the form

$$r=k[O_3]^a[Cellulose]^b$$

then, for a given ozone concentration,

$$\log(rate)=\log k'+b\cdot\log[cellulose]$$

Table 2. Summary of Ozone Kinetics Run Data

Run No.	Init. Ozone Conc., mg/L	Ozone Flow Rate, mL/min	Pulp Type	Consistency, %	Run Time, min	Init. Visc., cp	Final Visc., cp	$-dO_3/dt$, mg/L/min
27	15.1	90	Linter B	0.05	30	51	5.36	0.026
28	14.3	"	"	"	"	"	5.79	0.00
29	14.0	"	"	0.10	"	"	5.62	0.021
30	12.7	"	"	"	"	"	5.63	0.057
31	14.8	"	"	0.20	"	"	5.80	0.157
32	14.7	"	"	"	"	"	6.16	0.267
33	14.1	"	"	0.40	"	"	6.32	0.188
34	15.0	"	"	"	"	"	6.02	0.400
35	13.9	"	"	"	90	"	3.54	0.194
36	14.1	"	"	"	"	"	3.53	0.206
37[1]	14.5	"	"	"	"	"	3.49	0.276
38[1]	15.4	"	"	"	"	"	3.45	0.236
39	12.8	"	"	"	120	"	3.29	0.267
40	13.4	"	"	"	180	"	2.9	0.176
41	14.8	"	"	"	250	"	2.5	0.260
42	14.7	"	Linter C	"	30	58	5.41	0.386
43	10.2	"	"	"	"	"	7.04	0.283
44	11.1	"	"	"	"	"	7.2	0.287
45	20.2	"	"	"	"	"	4.9	0.455
46	20.9	"	"	"	"	"	4.71	0.567

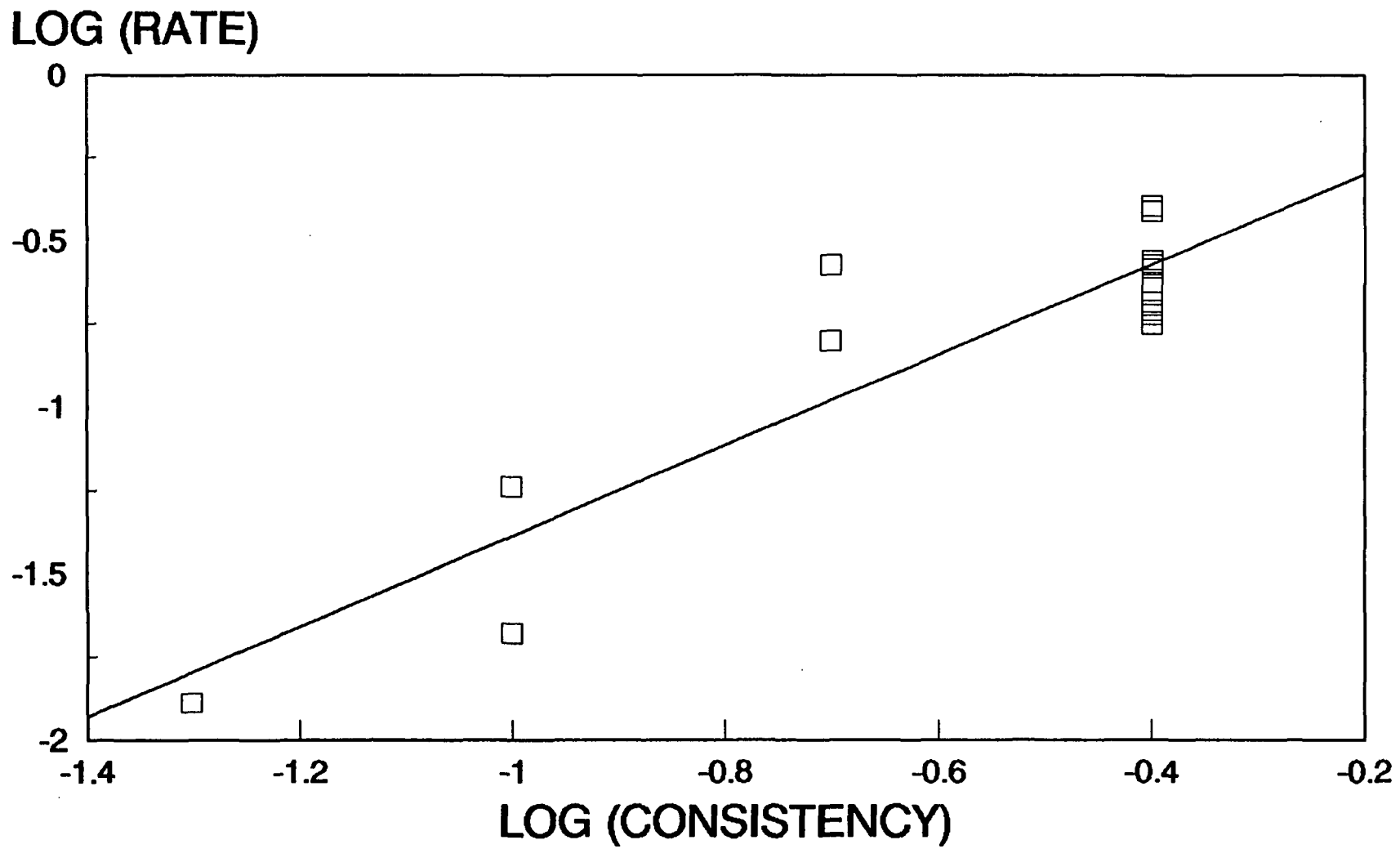
[1]Cotton linters not solvent extracted prior to run.

Figure 3 is a plot of log (initial rate) vs. log (consistency) for all runs in Table 2 having an initial ozone concentration of 14 ± 1.4 mg/L. The straight line fit has a slope of 1.37 ± 0.37, showing that the order in cellulose is very probably greater than one. This may indicate an interaction between reacting fibers, perhaps via dissolved reactive species. Figure 4 compares reactor outlet concentration-time profiles for reactions at three different consistencies.

Runs 35 and 36 are duplicate runs extended to a 1.5 hour reaction time, in an effort to observe the point at which the ozone concentration begins to recover. This point was not reached within the 1.5 hour reaction time. In runs 39, 40 and 41, the reaction time was

LOG (RATE) VS. LOG (CONSISTENCY)

(FIGURE 3)



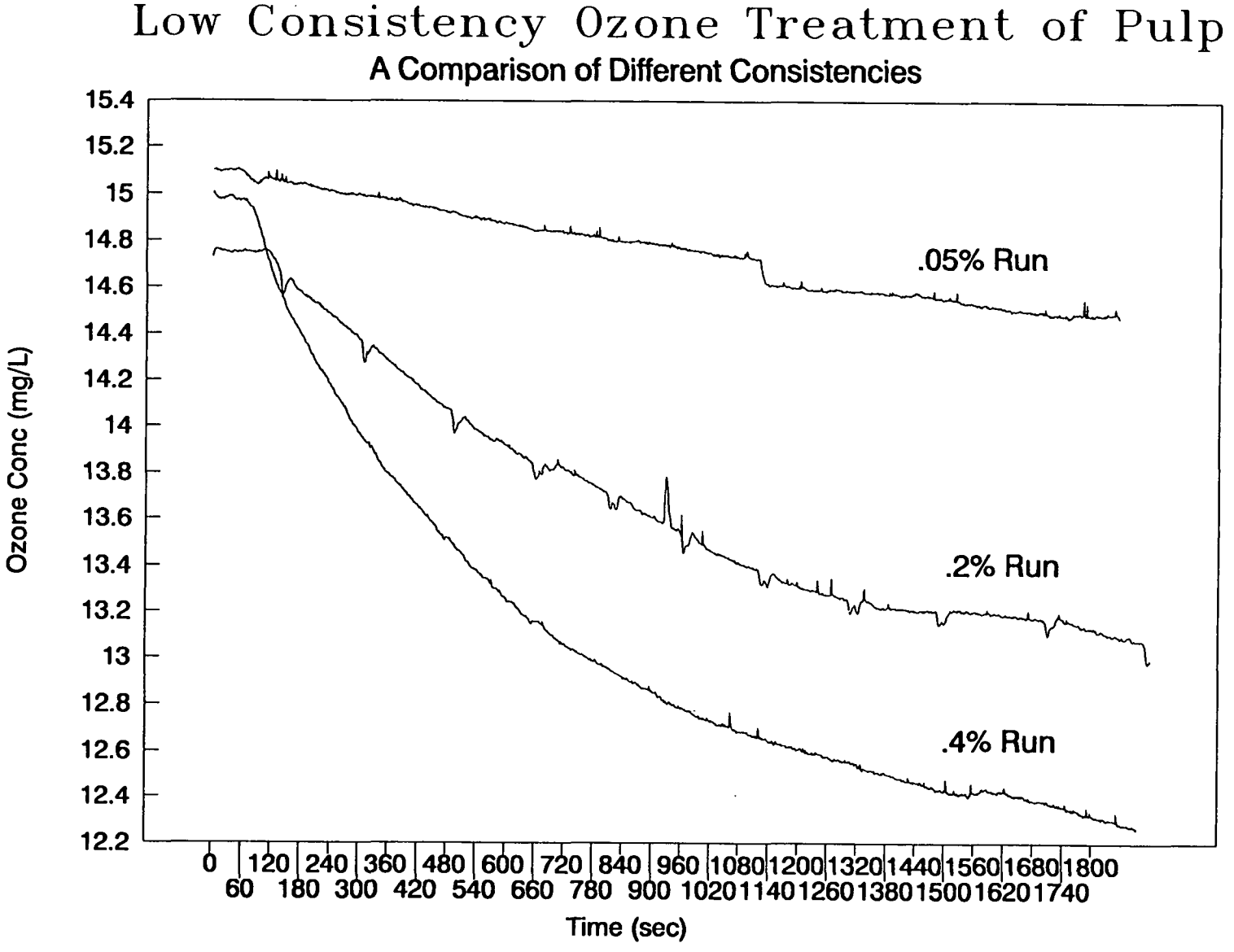

Low Consistency Ozone Treatment of Pulp
A Comparison of Different Consistencies
Ozone Conc (mg/L)
15.4
15.2
15
14.8
14.6
14.4
14.2
14
13.8
13.6
13.4
13.2
13
12.8
12.6
12.4
12.2
.05% Run
.2% Run
.4% Run
0 120 240 360 480 600 720 840 960 1080 1200 1320 1440 1560 1680 1800
60 180 300 420 540 660 780 900 1020 1140 1260 1380 1500 1620 1740
Time (sec)

FIGURE 4

further extended to as long as 4.5 hours. The 4.5 hour run reached a more or less constant ozone concentration after about one hour, showing only a weak tendency to increase beyond that point. This confirms earlier observations that cellulose continues to consume ozone over long periods of exposure.

Runs 37 and 38 were done to assess the effect of the solvent preextraction of the linters that has routinely been performed. There was no significant effect of omitting the extraction.

The final set of runs in Table 2, Runs 42 through 46, were done to assess the effect of varying the initial ozone concentration.

The order of the reaction with respect to ozone was estimated by plotting the logarithm of the observed initial rate against the logarithm of the initial ozone concentration. The resulting straight-line fit, shown in Figure 5, gives a value of 0.881 ± 0.40 for the order with respect to ozone. This may be compared to the values obtained earlier by analysis of viscosity data: 0.99 for the fast reaction and 0.81 for the parallel slow reaction.

Gas Dispersion in Medium Consistency Pulp

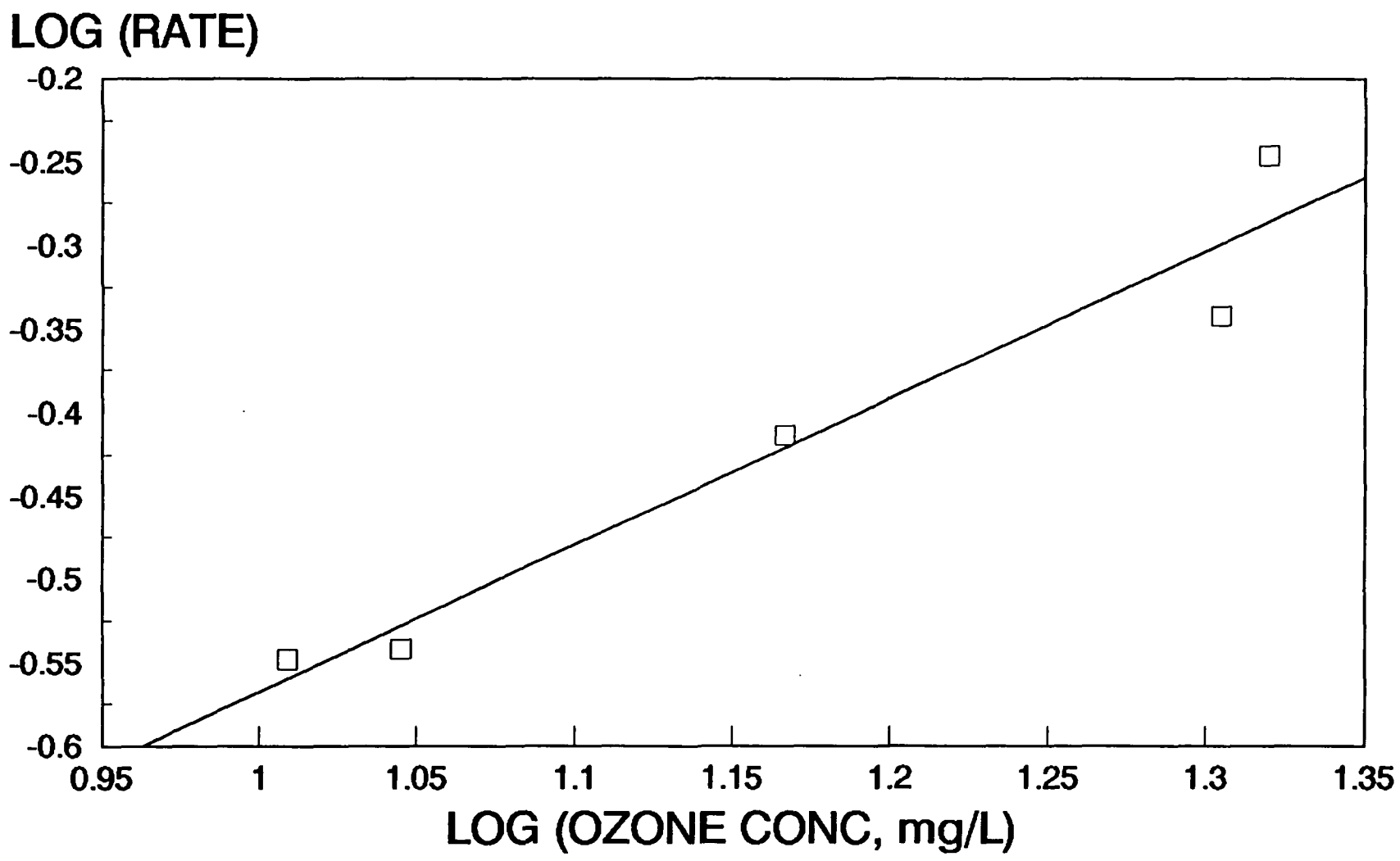
The dispersion of gases into medium consistency pulp is an important component of several bleaching processes, including oxygen delignification, ozone delignification, medium consistency chlorination, and oxygen-reinforced caustic extraction. We are studying the relevant mass transfer phenomena in a flow through laboratory fluidizing mixer, schematically depicted in Figure 6. The initial objective has been to determine the relationship between mixer operating variables and the amount of interfacial area generated. The latter quantity is estimated by measuring the amount of carbon dioxide absorbed by an alkaline pulp suspension. With this relationship in hand, it will be possible to repeat the experiments with other gases and relate the inferred interfacial area generation rate to relevant process performance factors.

During the previous reporting period we made the equipment operational, established operating procedures, and performed a fractional factorial experiment to relate gas transfer to mixer operating conditions. During the current reporting period, we have refined the procedure to take into account consistency changes that occur during operation of the mixer and have completed a more comprehensive factorial experiment. Subsequent data analysis has yielded a simple relationships describing the behavior of the mixer as a gas disperser. In addition to providing a basis for interpretation of future experiments, these relationships provide insight relevant to the operation of commercial medium consistency gas dispersion systems.

A complicating factor in the earlier experiments was the tendency of the pulp to dewater in the reservoir column feeding the mixing chamber. The result was that the consistency of the pulp issuing from the mixing chamber tended to increase with time. Since the first half of each run represented transient operation and was discarded, the part of the run from which data was taken corresponded to a consistency higher than that of the initial

LOG (RATE) VS. LOG (OZONE CONC, mg/L)

(FIGURE 5)



Flow-through Fluidizing Mixer

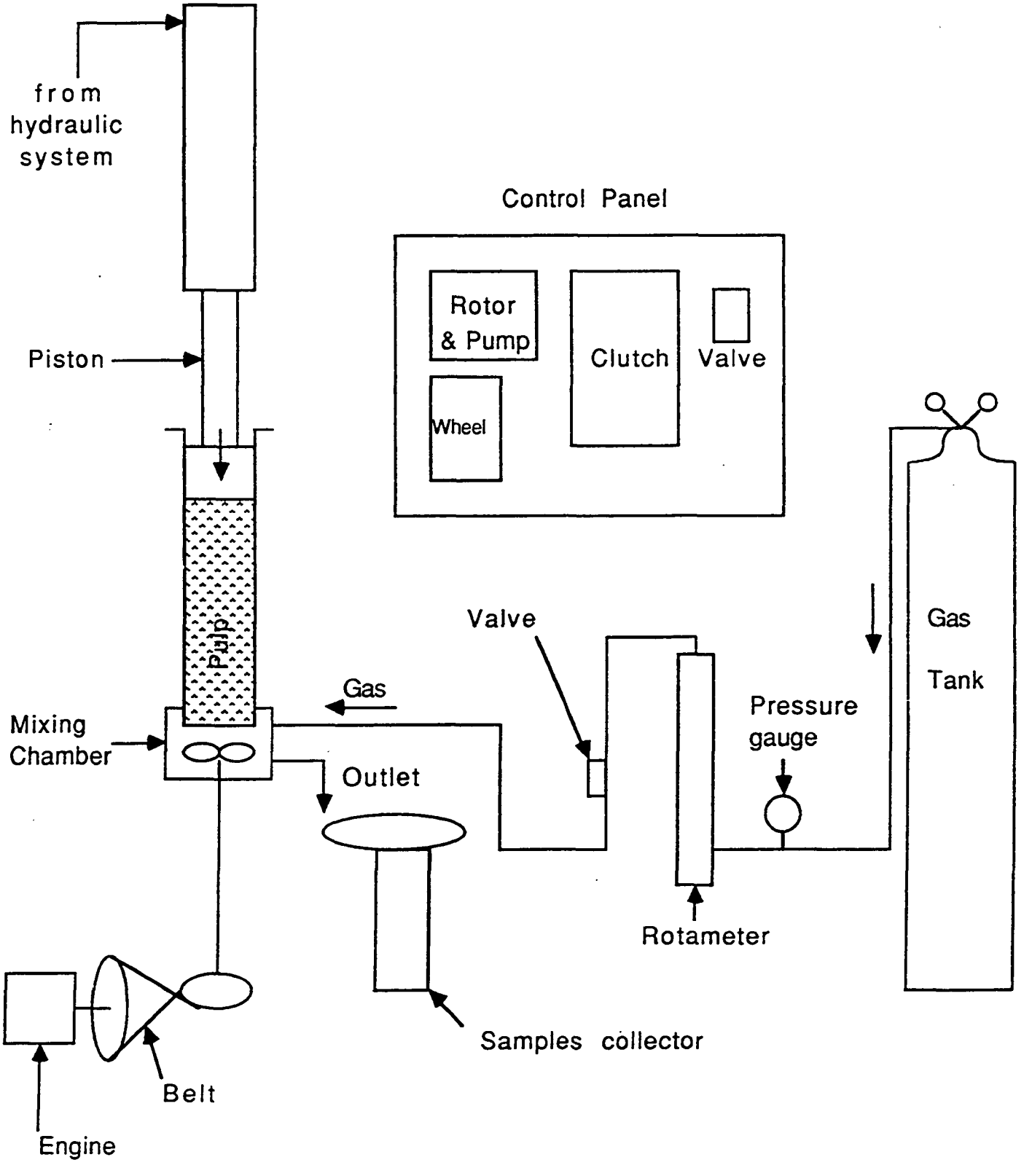


Figure 6

pulp. To account for this in the more recent experiments, we have separately determined the consistency of the pulp issuing from the mixer during the part of each run during which gas absorption data was taken. A corrected gas charge was then calculated by dividing the mass flow of gas to the mixing chamber by the mass flow of dry pulp issuing from the mixing chamber.

The results of all relevant experiments are given in Table 3. The structure of Table 3 approximates that of a factorial experiment, with replication of alternate treatment combinations.

Table 3. Dispersion of Carbon Dioxide in Medium Consistency Hardwood Kraft Pulp

Run No.	consistency initial pulp (%)	consistency mised pulp (%)	rotor speed (RPM)	piston speed (in/s)	gas flow (g/s)	gas charge (%)	pulp flow (g/s)	CO2 abs (mole /100g of dry pulp)
1	9.72	9.72	2150	1.96	0.1	0.52	19.1	10.6
2	8.46	9.31	1750	2.01	0.1	0.54	18.5	8.0
3	11.54	11.18	1750	2.00	0.1	0.36	27.5	4.2
4	9.70	9.66	3560	1.96	0.1	0.61	16.5	13.4
5	8.59	9.91	3250	2.01	0.1	0.50	19.9	9.4
6	10.15	10.69	3250	1.96	0.1	0.37	26.9	7.1
7	9.70	10.05	2150	4.88	0.25	0.60	41.7	5.6
8	8.72	9.78	1750	4.95	0.25	0.52	47.7	5.0
9	11.18	11.07	1750	4.95	0.25	0.44	56.5	4.8
10	9.15	9.76	3560	5.00	0.25	0.55	45.2	6.9
11	8.58	9.71	3510	4.87	0.25	0.51	49.4	9.9
12	11.07	10.25	3250	4.91	0.25	0.38	65.1	9.8
13	8.95	8.93	2150	1.97	0.4	2.57	15.6	18.9
14	8.45	9.47	1750	2.01	0.4	2.31	17.3	15.1
15	10.54	10.09	1750	1.97	0.4	1.65	24.3	11.7
16	9.23	9.92	3560	1.97	0.4	2.81	14.2	17.7
17	8.75	9.08	3250	2.01	0.4	3.08	13	18.1
18	10.5	10.74	3250	1.96	0.4	1.56	25.6	18.2
19	9.60	9.91	2150	4.91	0.63	1.40	44.9	12.3
20	8.93	9.94	2150	4.91	0.63	1.31	48.0	10.6
21	11.33	11.22	1750	4.95	0.63	0.98	64.3	14.1
22	9.18	9.64	3560	4.95	0.63	1.44	44.0	14.6
23	9.06	10.1	3560	5.00	0.63	1.31	48.1	14.7
24	11.22	10.76	3250	4.91	0.63	0.92	68.1	11.3

Because replication was only partial, and because the levels of the independent variables did not exactly correspond to their factorial levels, the data were analyzed by multiple regression instead of by analysis of variance. The independent variables in the regression were as follows:

A = coded consistency = actual consistency, % - 10
B = coded rotor speed = (actual rotor speed, rpm - 2500)/750
C = coded piston speed = (actual piston speed, in/s - 3.5)/1.5
D = coded gas charge = (actual gas charge, % - 1.25)/0.75

After discarding two outlying data points (no. 18 and no. 21), the following simple equation was found to explain 83% of the variation in the data:

$$Y = 11.1 + 1.3B + 3.2D$$

where Y = CO_2 absorbed, mmol/100 g dry pulp.

According to this equation the rate of gas absorption is increased by increasing the rotor speed, the gas charged to the mixer, or both, but is unaffected by pulp consistency or by the rate of pulp flow through the mixer. The lack of consistency effect may indicate that the pulp is fully fluidized over the range of consistency investigated. The lack of a retention time effect suggests that the gas-pulp dispersion is fully formed immediately upon entry into the mixing zone, and that bubble size is determined by shear rate alone; at a given shear rate initially large bubbles are not reduced in size with increased retention time. Practical implications are that minor consistency fluctuations should not affect mixer performance, and that the mixing zone can be very small in relation to production rate.

Further analysis showed that the addition of two more terms to the above equation could be statistically justified, even though the additional terms were of considerably smaller importance than the main effects of rotor speed and gas charge. The resulting equation explained 91% of the variation in the data:

$$Y = 11.4 + 1.4B + 3.7D + 1.9AC + 1.3CD$$

The AC term in this equation indicates that increased pulp flow rate decreases gas transfer at low consistency, but increases it at high consistency. The decrease at low consistency suggests the existence of a minor time dependent bubble comminution effect, while the increase at high consistency may reflect the existence of "dead zones" within the mixer, for example, upstream of the baffles. The size of these dead zones may be expected to diminish with increased rate of flow of pulp through the mixing zone.

The CD term indicates that the positive effect of gas charge is greater at high pulp flow rate than at low pulp flow rate. In other words, an incremental gas addition is more effectively captured at high pulp flow rate. This is another indication of the existence of dead zones of a size that is decreased when pulp flow is increased.

Catalysis of Peroxide Delignification

A model system has been developed to study the effect of catalysts on the selectivity of hydrogen peroxide delignification. Lignin and carbohydrate are represented by polymeric model substances. Molecular mass changes are measured by size exclusion chromatography and by viscometry. A chemiluminescence assay is used to monitor the production of hydroxyl radicals. The system has been used to show that the carbohydrate model is less severely degraded in the presence of Fe(II)-EDTA than in the presence of Fe(II). In addition, fewer hydroxyl radicals are generated in the former system.

A complete report by C. Walker is appended.

AOX Characterization

Recent work has included comparative characterizations of chlorinated organic matter produced by treatment of oxygen bleached softwood kraft pulp with chlorine and chlorine dioxide. The two classes of material differ sharply in amount and character. A complete report by T. Schwantes is appended.

Mixing Effects

We reported earlier that poorly mixed chlorination stages gave much higher levels of AOX than well-mixed stages, when both were conducted to the same post-extraction kappa number. At that time, it was recognized that information on effects of mixing on chlorophenols generation would also be of interest, so a new series of experiments was planned to generate samples for this purpose. This was also seen as an opportunity to corroborate the observed effect on AOX, especially in view of its apparently large magnitude. The unexpectedly low AOX values for the well-mixed chlorinations also appeared to be in need of confirmation.

To provide independent confirmation of the earlier data, it was decided to use a different method for AOX determination. The earlier data were obtained by EPA method 9020, which employs adsorption on carbon columns. The batch method, SCAN-W 9:89 was chosen for the new experiments. To avoid complications due to varying degrees of loss of volatile materials, the more recent experiments were also done under conditions designed to minimize loss of volatiles.

The chlorination stage was conducted in a Quantum Technologies laboratory mixer/reactor. A 120 g sample of unbleached pulp (softwood kraft, kappa no. 27.8, viscosity 25.9 cp.) was chlorinated for 30 minutes at 45 deg. C and 4% consistency. Mixing was either good (180 sec. at 30 Hz) or poor (13 sec at 1 Hz). A one-liter effluent sample was withdrawn from the reactor through a cold trap before the reactor was opened. It was then transferred immediately to a sealed container and stored cold.

Subsequently, the reactor was opened and the pulp was removed and thickened to the point at which 20% of the liquid phase present in the chlorination stage remained with the pulp, to be carried over into the extraction stage.

The caustic extraction stage was conducted in sealed Kapak bags on 40 g samples of chlorinated pulp for 60 minutes at 70 deg. C and 10% consistency. The NaOH charge was calculated as $(\%Cl_2)(0.55) + (.05)(20 - 100[\text{Kappa Factor}])$. Effluent was collected by cooling the bag to ice temperature before opening it and squeezing out and filtering full strength effluent. The pH of the sample was adjusted to 2 with concentrated nitric acid and stored cold.

Experiments were conducted at kappa factors of 0.05, 0.10 and 0.20 under conditions of both poor and good mixing. Two to four replicates were done at each condition. The resulting data are shown in Table 4 and are plotted against post-extraction kappa number in Figure 7. For comparison, the data obtained with the EPA method, and without taking special precautions to preserve vb volatiles, are shown in Figure 8. The poor mixing data are similar for the two cases, but AOX levels for good mixing are generally higher in the more recent data, especially at intermediate kappa numbers. The more recent data confirm the earlier conclusion that improved mixing gives significant reductions in AOX, although the reductions may be less than indicated earlier. The recent data more clearly show that good mixing becomes more important as the CE kappa number is decreased.

In attempting to explain the discrepancy between the two sets of data, we considered the possibility of nonrepresentative sampling in the newer data, since sampling through the cold trap limited the fraction of the total liquid phase present that could be included in the sample. Additional experiments were therefore done to determine within-sample AOX variation when sampling through the cold trap. In the first such experiments, a 0.2 kappa factor chlorination was done under poorly mixed conditions and effluent samples, each about 250 mL, were successively drawn though the cold trap until no more could be taken. Each of the resulting six samples was then analyzed in duplicate for AOX.

The resulting data are plotted against sample order number in Figure 9. They show that the last samples withdrawn had significantly higher AOX concentration than the first samples.

The variation between samples was expected, because of the poor mixing, but the systematic nature of the trend was unexpected. It is not clear whether this is a general phenomenon or just a fortuitous occurrence in this particular experiment. More to the point, the observed 20% variation suggests that nonrepresentative sampling may have contributed to underestimation of the magnitude of the mixing effect in the recent data.

The corresponding experiment conducted under conditions of good mixing gave the data in Figure 10. The AOX level was lower and more constant than in the poorly mixed case. Note, however, that, as shown in Table 4, the pulp from this chlorination released more AOX in the extraction stage than did the pulp from the poorly mixed experiment.

CHLORINATION STAGE

Bleaching Number	Replicate Number	Mixing Quality	Kappa Factor	Exit pH	Residual (g/l CL2)	AOX Discharge (Kg/ODMT) Test A	Test B	AVG.
6	1.000	Poor	0.050	2.310	0.000	0.240	0.250	0.245
9	2.000			2.420	0.000	0.496	0.496	0.496
1	1.000	Good	0.050	2.160	0.000	0.180	0.196	0.188
7	2.000			2.330	0.000	0.200	0.191	0.196
8	1.000	Poor	0.100	2.200	0.000	0.393	0.463	0.428
12	2.000			1.950	0.000	0.540	0.577	0.559
3474-4126MC0017.10P	3.000			2.330	0.000	0.525	0.565	0.573
						0.678	0.622	
						0.525	0.525	
2	1.000	Good	0.100	2.180	0.000	0.372	0.380	0.376
10	2.000			1.950	0.020	0.496	0.502	0.499
3474-4126MC0016.10G	3.000			2.120	0.000	0.413	0.440	0.430
						0.403	0.380	
						0.530	0.413	
3	1.000	Poor	0.200	1.980	0.160	3.457	3.250	3.354
11	2.000			1.810	0.210	1.907	1.700	1.804
3474-4126MC0014.20P	3.000			1.990	0.300	2.000	1.880	2.246
						2.250	2.250	
						2.130	2.250	
						2.410	2.360	
						2.290	2.230	
						2.470	2.430	
4	1.000	Good	0.200	1.880	0.050	0.940	1.047	0.994
5	2.000			1.850	0.090	2.307	2.333	2.320
3474-4126MC0013.20G	3.000			1.870	0.070	2.753	2.520	2.637
3474-4126MC0015.20G	4.000			1.730	0.280	1.790	1.770	1.760
						1.710	1.720	
						1.700	1.780	
						1.690	1.690	
						1.860	1.870	
						1.770	1.770	

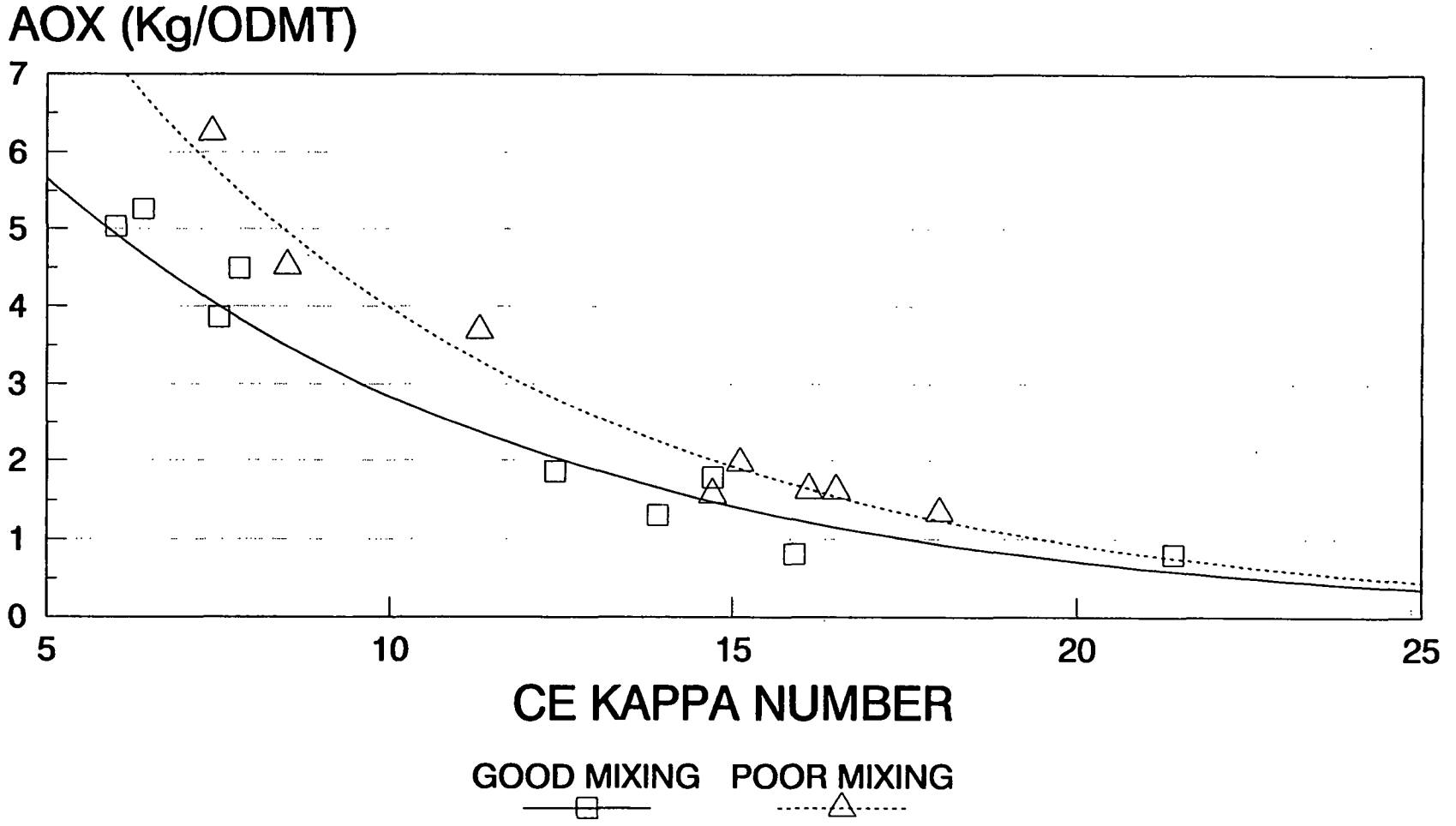
EXTRACTION STAGE

Bleaching Number	% NaOH	Exit pH	AOX Discharge (Kg/ODMT) Test A	Test B	AVG.	AOX TOTAL (Kg/ODMT)	CE Kappa
6.000	1.520	11.200	1.290	1.482	1.386	**1.631**	16.100
9.000	1.520	11.300	0.742	0.949	0.846	**1.342**	18.000
1.000	1.520	11.300	0.610	0.624	0.617	**0.805**	21.400
7.000	1.520	11.300	0.587	0.655	0.621	**0.817**	15.900
8.000	2.030	11.300	1.517	1.560	1.539	**1.967**	15.100
12.000	2.030	11.200	1.101	1.023	1.062	**1.621**	16.500
3474-4126MC0017.10P	1.930	11.200	0.967	1.031	0.999	**1.572**	14.700
2.000	2.010	11.400	1.412	1.412	1.412	**1.788**	14.700
10.000	2.030	10.700	1.502	1.203	1.353	**1.852**	12.400
3474-4126MC0016.10G	1.930	11.400	0.896	0.868	0.882	**1.312**	13.900
3.000	3.060	11.200	2.874	2.931	2.903	**6.256**	7.400
11.000	3.060	11.100	2.461	2.677	2.569	**4.373**	8.500
3474-4126MC0014.20P	2.870	11.300	1.430	1.480	1.455	**3.701**	11.300
4.000	3.060	11.300	2.945	2.786	2.866	**3.859**	7.500
5.000	3.060	11.000	2.706	3.174	2.940	**5.260**	6.400
3474-4126MC0013.20G	2.870	11.300	2.316	2.472	2.394	**5.031**	6.000
3474-4126MC0015.20G	2.870	11.300	2.750	2.710	2.730	**4.490**	7.800

Table 4. AOX Generation Under Conditions of Poor and Good Mixing

AOX CONCENTRATION (Kg/ODMT) Vs. CE KAPPA NUMBER

(Figure 7)



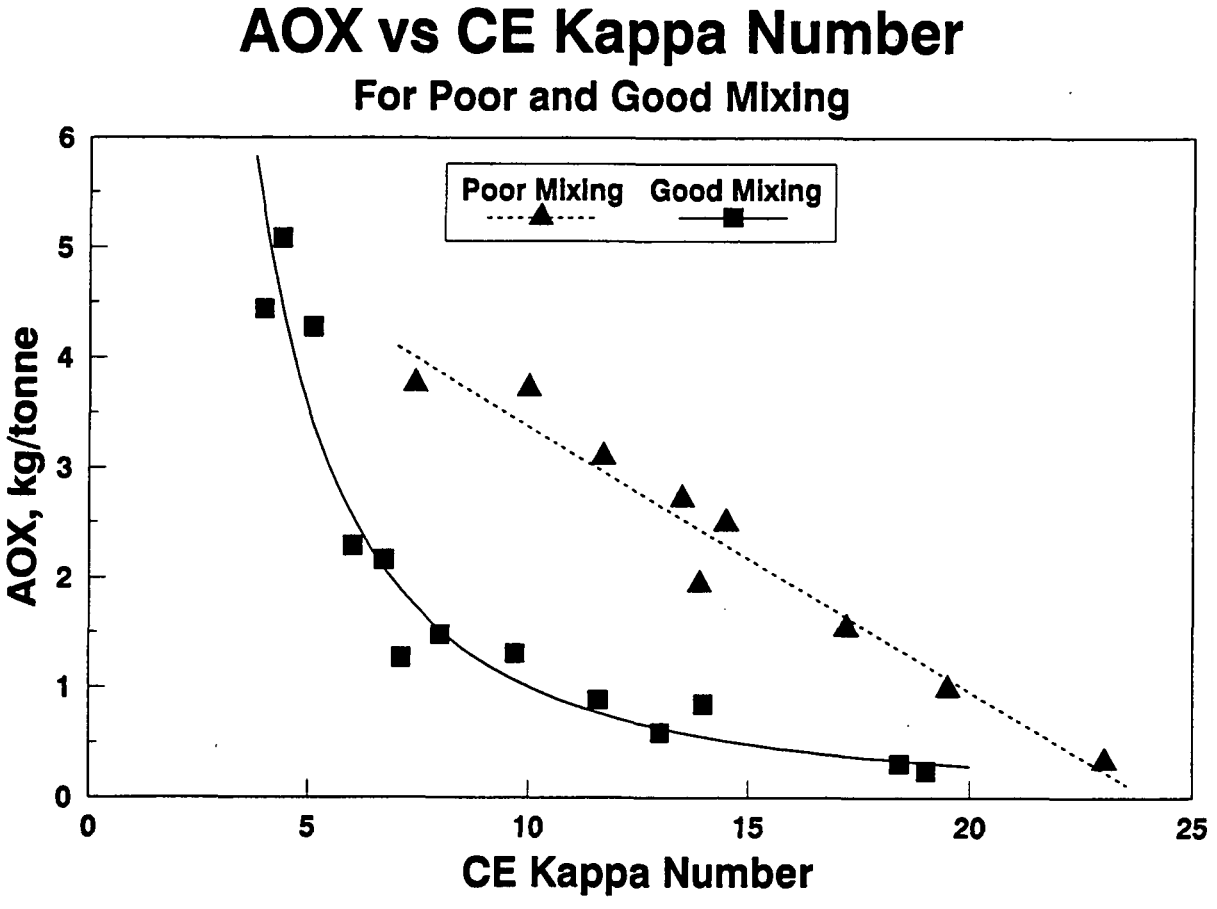
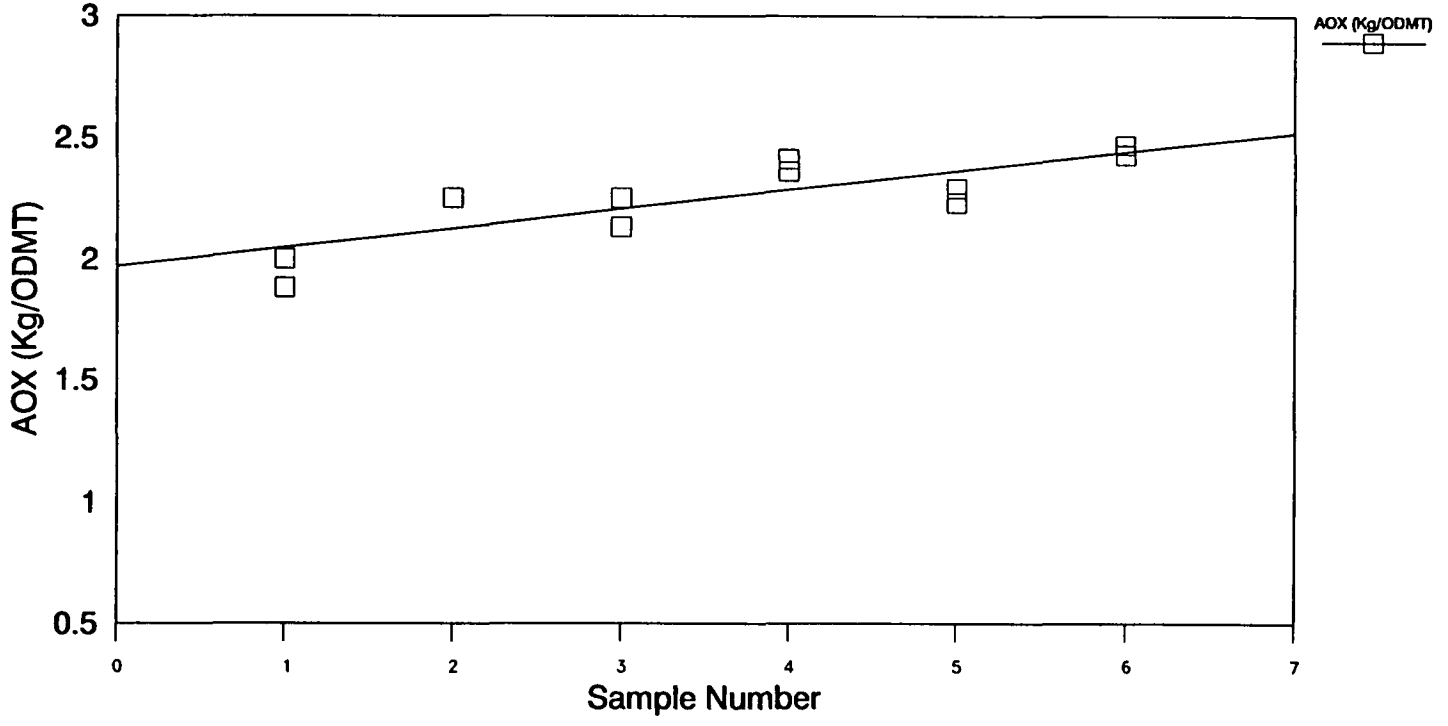


Figure 8. Effect of mixing on AOX generation - earlier data.

AOX Analysis of C-Stage Effluent

0.2 Chlorine Multiple (Poor Mixing)

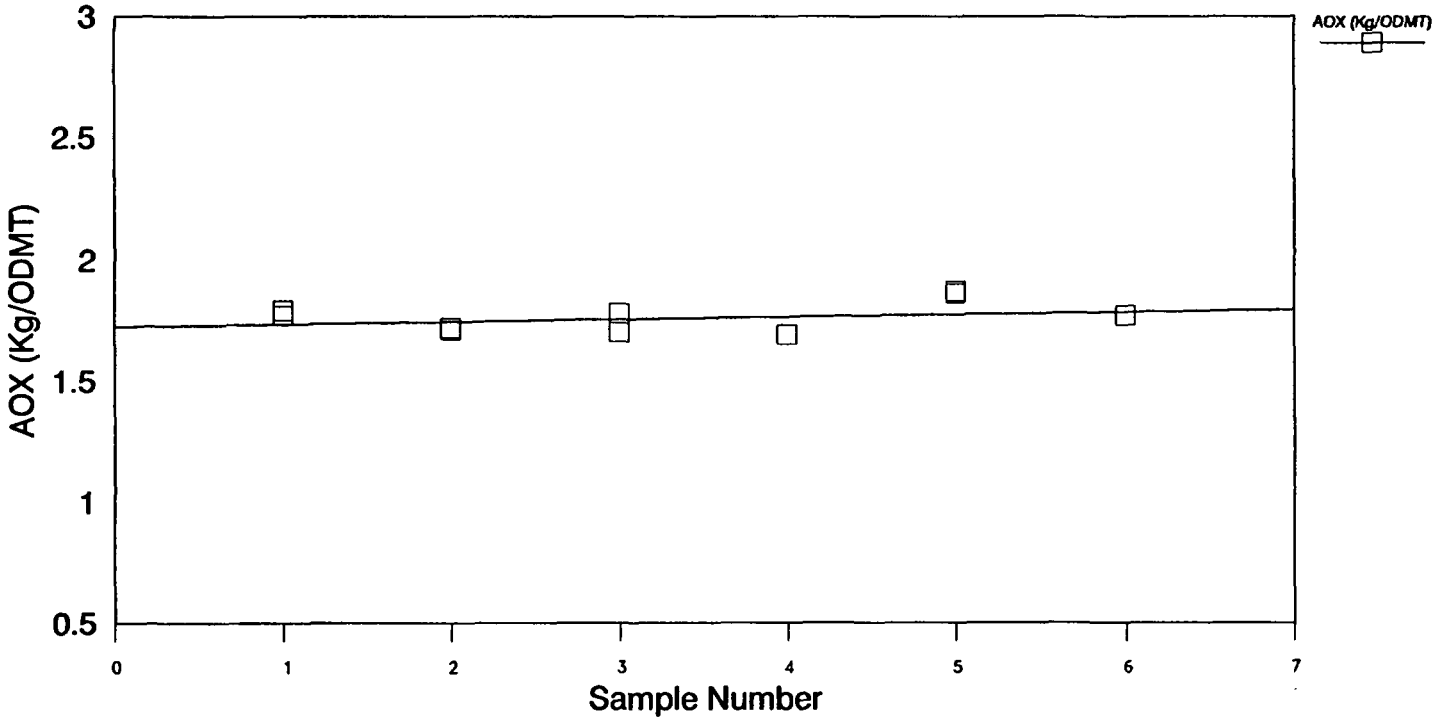
(Figure 9)



AOX Analysis of C-Stage Effluent

0.2 Chlorine Multiple (Good Mixing)

(Figure 10)



Figures 11 and 12 show the results of similar experiments run at 0.1 kappa factor. The poorly mixed sample again showed substantial variation, but in this case no trend was apparent. The well mixed sample showed little variation if a high result from a single test is discounted.

The discrepancy between earlier and current determinations of the effect of mixing on AOX can only be partially explained by non representative sampling of the poorly mixed C-stage effluent. A better understanding of this situation is needed, largely because the explanation, once found, is likely to have practical implications. Among the possibilities being considered are mixing-related changes in AOX character that respond differently to a change in AOX test method, and mixing effects on the proportion of AOX that is volatile.

FUTURE WORK

The following work is planned:

1. Determination of rate laws for ozone degradation of cellulose, including effects of ozone concentration, pulp consistency, degree of polymerization, and the influence of other pulp components. The last will be determined by comparative studies of cotton linters, bleached pulps, and unbleached pulps, as well as by additions of lignin or hemicellulose. Factors affecting the extent and duration of the initial, rapid phase of degradation will be identified and studied.

2. Results to date on lignin structure and bleachability will be collected, reviewed and published. The influence of phenolic hydroxyl groups and α-carbonyl groups will be determined by manipulating their contents in unbleached pulp, analyzing the pulp and observing associated effects on ease of lignin removal in nonchlorine and chlorine dioxide bleaching stages.

3. Results on dispersion of gas into medium consistency pulp will be analyzed and a publication written.

4. The effects of different catalysts on the relative rates of peroxide oxidation of polymeric lignin and cellulose models will be measured. Associated effects on hydroxyl radical generation will be monitored (Ph.D. thesis research - C. Walker).

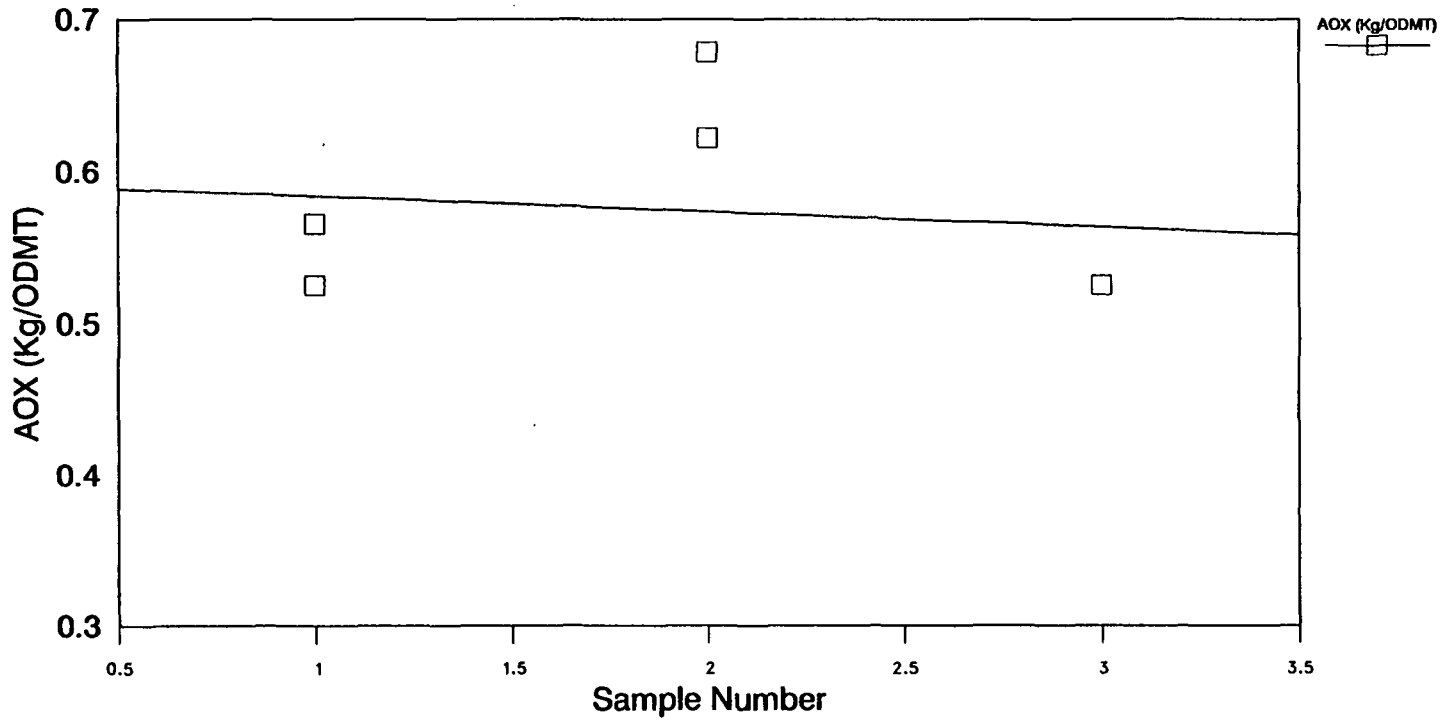
5. Effects of high substitution bleaching process variables on the nature and amounts of chlorinated organic byproducts will be determined (Ph.D. thesis research - T. Schwantes).

6. Results obtained to date on effects of mixing in chlorination will be organized into a publication. The work will be extended to include effects on chlorophenols and effects of substituting chlorine dioxide for chlorine.

AOX Analysis of C-Stage Effluent

0.1 Chlorine Multiple (Poor Mixing)

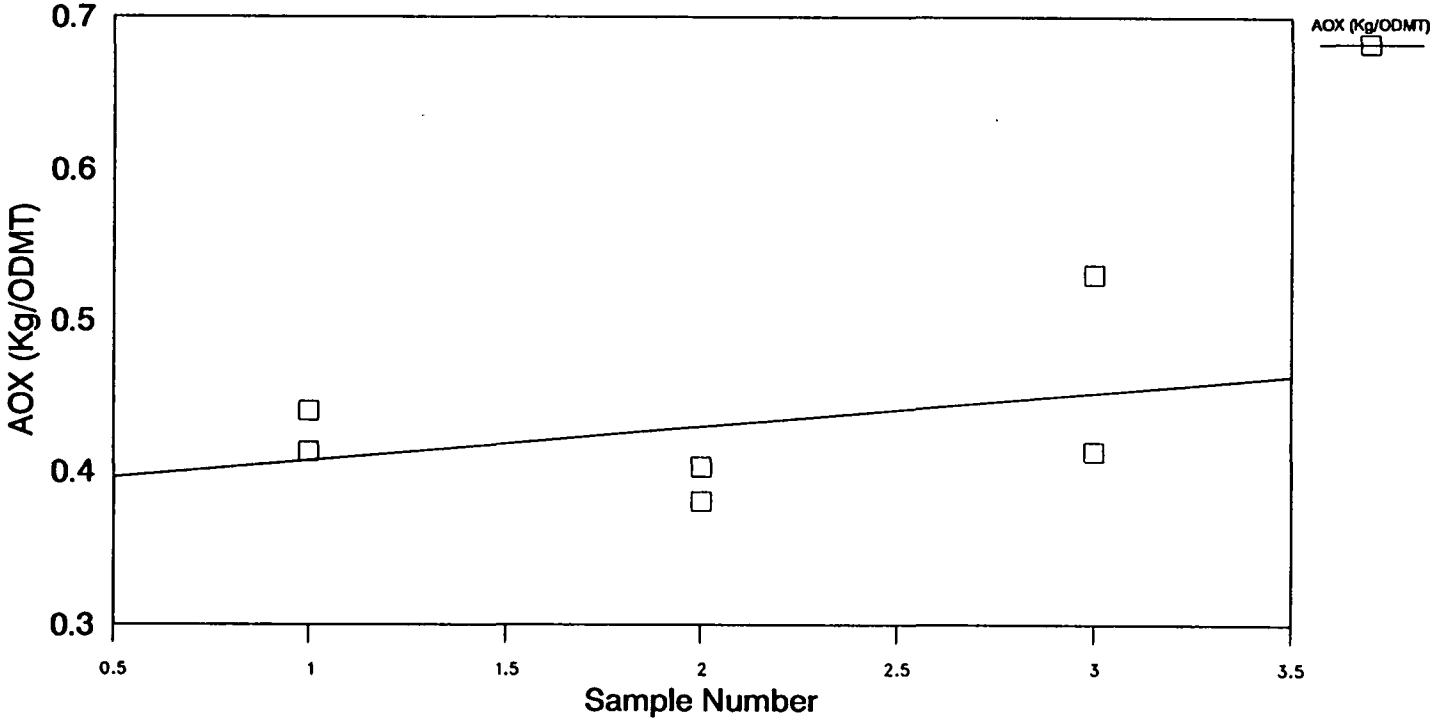
(Figure 11)



AOX Analysis of C-Stage Effluent

0.1 Chlorine Multiple (Good Mixing)

(Figure 12)



7. The bleaching effectiveness of cyclic peroxides, in particular DMD, will be evaluated in several nonchlorine bleaching sequences.

8. Isolation of lignin from unbleached, oxidatively pretreated, and enzymatically pretreated pulps for studies of structural features will be further pursued. Methods will include the use of cellulase-hemicellulase mixtures and mild acid hydrolysis.

9. Phenomenological studies of medium consistency ozone bleaching sequences will be conducted, with the aim of developing new ozone bleaching technology.

10. Consideration will be given to studies of extended delignification and effects of unconventional processing on pulp physical properties as manpower becomes available.

SECTION 1

DEVELOPMENT OF BIOMIMETIC APPROACH TO PULP BLEACHING

Colleen C. Walker
Ph.D. Candidate

DEVELOPMENT OF A BIOMIMETIC APPROACH TO PULP BLEACHING

Colleen C. Walker, PhD Candidate

Thesis Committee: **Dr. Ronald Dinus**

Dr. Karl-Erik Eriksson (Univ. of Ga., Athens)

Dr. Thomas McDonough

SUMMARY

A model system has been developed to study the effect of iron catalysts on the selectivity of hydrogen peroxide delignification. Iron complexes in the presence of hydrogen peroxide, which "mimic" the lignin-degrading enzyme ligninase, will be compared to the Fenton system [Fe(II) + H2O2]. Lignin and carbohydrate are represented by polymeric model compounds, lignosulfonate and hydroxyethyl cellulose (HEC), respectively. Molecular weight changes in lignosulfonate are measured by High Performance Size Exclusion Chromatography (HPSEC). Molecular weight changes in HEC are measured using intrinsic viscosity measurements and the Mark-Houwink relationship. A chemiluminescence assay is used to monitor the production of hydroxyl radicals in reaction solutions. Careful selection of reactions conditions is essential as this assay alters reaction rates under certain conditions. Experiments with HEC and H2O2 in the presence of Fe(II) and Fe(II)-EDTA indicate that degradation of the HEC is less severe in the H2O2/Fe(II)-EDTA system. This system produces fewer hydroxyl radicals than the H2O2/FeSO4 system.

INTRODUCTION

In the presence of hydrogen peroxide the enzyme ligninase, isolated from white-rot fungi, has been used to bleach softwood kraft pulp. Unfortunately, mill process temperatures often exceed those necessary to maintain high enzymatic activity. Although commercial application of ligninases is limited, systems which mimic this enzyme are more practical. Ligninase has a protoporphyrin prosthetic group; compounds with such a porphyrin structure have been used to elucidate the mechanism for the ligninase degradation. Many of these biomimetic compounds have been able to cleave the Ca-Cb bound in lignin model compounds. Preliminary research efforts have shown that porphyrin-like substances, i.e. hemoglobin, in the presence of hydrogen peroxide mimics the action of ligninase.

Laboratory experiments using this biomimetic approach for pulp bleaching have produced promising results; Pettersson, et al.[1] found that reductions in Kappa number and viscosity for a biomimetically bleached pulp were equal to that of an oxygen bleached pulp. Carbohydrate losses in biomimetically bleached pulps are sometimes high, attributable to the non-selectivity of these systems.

Previous work has established that hydroxyl radicals do not participate in the degradation of lignin by the enzyme

ligninase.[2] Hydroxyl radicals are produced in the presence of hydrogen peroxide and biomimetic compounds.[3,4,5] However, the relative selectivity of these systems are not known. The objective of this thesis is to examine three biomimetic systems for their selectivity for lignin over carbohydrate. The second segment of this thesis will be to modify the most selective catalyst to increase its affinity for lignin-like structures.

EXPERIMENTAL APPROACH

Three different types of biomimetic compounds, Fe (II), EDTA-Fe(II) and a ferrous porphyrin, will be evaluated for their preference for the lignin model over the carbohydrate model. Hydrogen peroxide will be used as the oxidant for all experiments. A chemiluminescence assay has been selected to monitor the production of hydroxyl radicals in these systems.

A residual lignin model compound was desired, which would be soluble in aqueous solution, to maintain homogeneous reaction conditions. Lignosulfonate, which is soluble in aqueous solutions, has been chosen as the lignin model compound. High Performance Size-Exclusion Chromatography (HPSEC) is used to evaluate molecular weight changes in the lignosulfonate.

Hydroxyethyl cellulose (HEC) has been chosen as the carbohydrate model compound. HEC maintains a constant viscosity for pH 2 - 10, an ideal quality for experiments in which pH is a variable. The molecular weight change of HEC can be determined from capillary viscometer measurements and published correlations between molecular weight of HEC and intrinsic viscosity.[6]

The reactor system used for these experiments has been designed so that the amount of hydrogen peroxide consumed by chemical reaction as well as catalytic decomposition can be measured. As hydrogen peroxide decomposes into oxygen, the evolved gas can be measured without pressurizing the reaction vessel. Residual hydrogen peroxide is determined by iodometric titration. The amount of hydrogen peroxide consumed by reaction is determined by subtracting the residual and decomposed hydrogen peroxide from the original amount. Rates of hydrogen peroxide decomposition and reaction with substrate can then be calculated from these measurements.

RESULTS AND DISCUSSION

Chemiluminescence Assay for Detecting Hydroxyl Radicals

Many analytical techniques are available for quantitatively measuring hydroxyl radicals, but these techniques often require synthesis of the active substrate or involve significant capital expenditure. The chemiluminescence assay developed by Reitberger and Gierer[7] measures the amount of light produced from the oxidation of hydroxylated phthalic

hydrazide (HPH). Phthalic hydrazide, a commercially available chemical, is directly added to reaction solutions. Once hydroxylated by hydroxyl radicals, a separate oxidation step performed on a reaction sample produces chemiluminescence from HPH. Light is measured by a photometer using a data acquisition system.

To verify the validity of the chemiluminescence assay, reaction conditions were selected in which hydroxyl radicals were known to be produced: 100 mM H2O2, 10 mM Fe(II)-EDTA at pH 3.0. The concentration of Fe(II)-EDTA was varied to examine the sensitivity of this assay. Figure 1 shows results from these experiments. As the concentration of Fe(II)-EDTA increases, the chemiluminescent yield also increases.

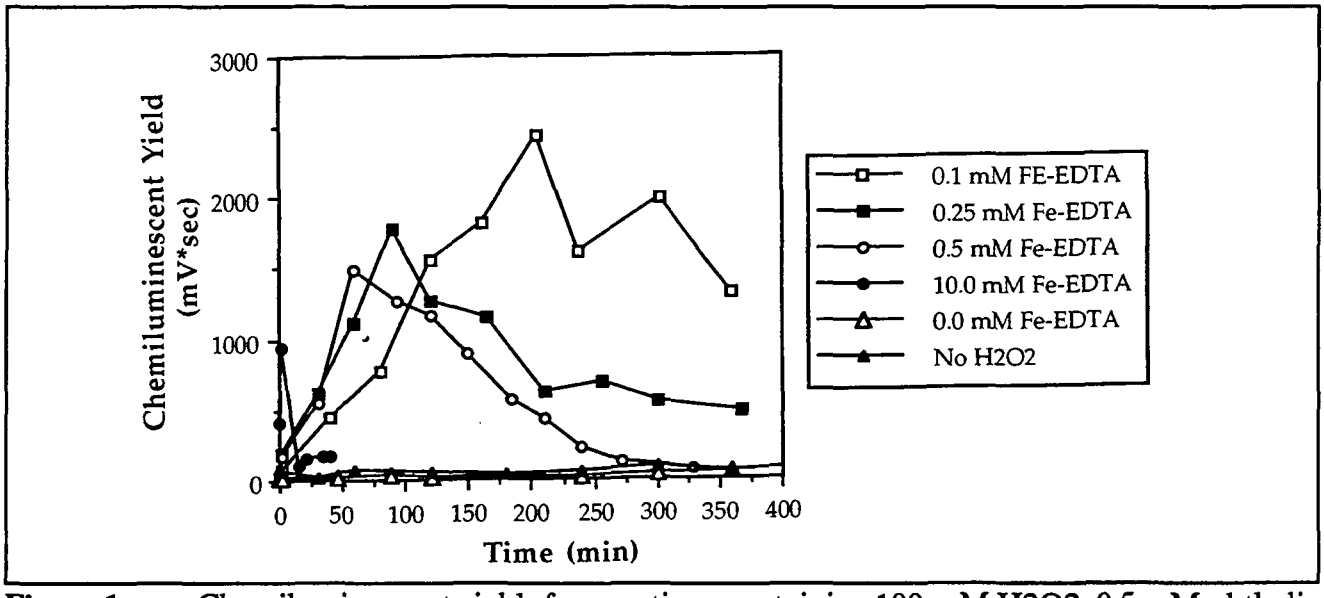


Figure 1 Chemiluminescent yields for reactions containing 100 mM H2O2, 0.5 mM phthalic hydrazide with varying concentrations of Fe(II)-EDTA at pH 3.0 and 45C.

In Figure 1 a decline in the chemiluminescent yield is observed in all reactions. This decline was attributed to degradation of the phthalic hydrazide. All available phthalic hydrazide (0.5 mM for these reactions) was hydroxylated by hydroxyl radicals. Any additional radicals produced then proceeded to attack the phthalic hydrazide to render it non-chemiluminescent. This hypothesis was later verified by studying the chemiluminescent yield for solutions containing 100 mM H2O2 and 0.5 mM phthalic hydrazide irradiated with UV light. Irradiation of H2O2 solutions produces hydroxyl radicals. Figure 2 shows the chemiluminescent yield from this reaction. An increase in yield is seen for the first 90 minutes, followed by a decline.

The concentration of phthalic hydrazide present in reaction solutions affected the rate of hydrogen peroxide decomposition. Figure 3 shows that hydrogen peroxide decomposition is stabilized by increasing concentrations of phthalic hydrazide.

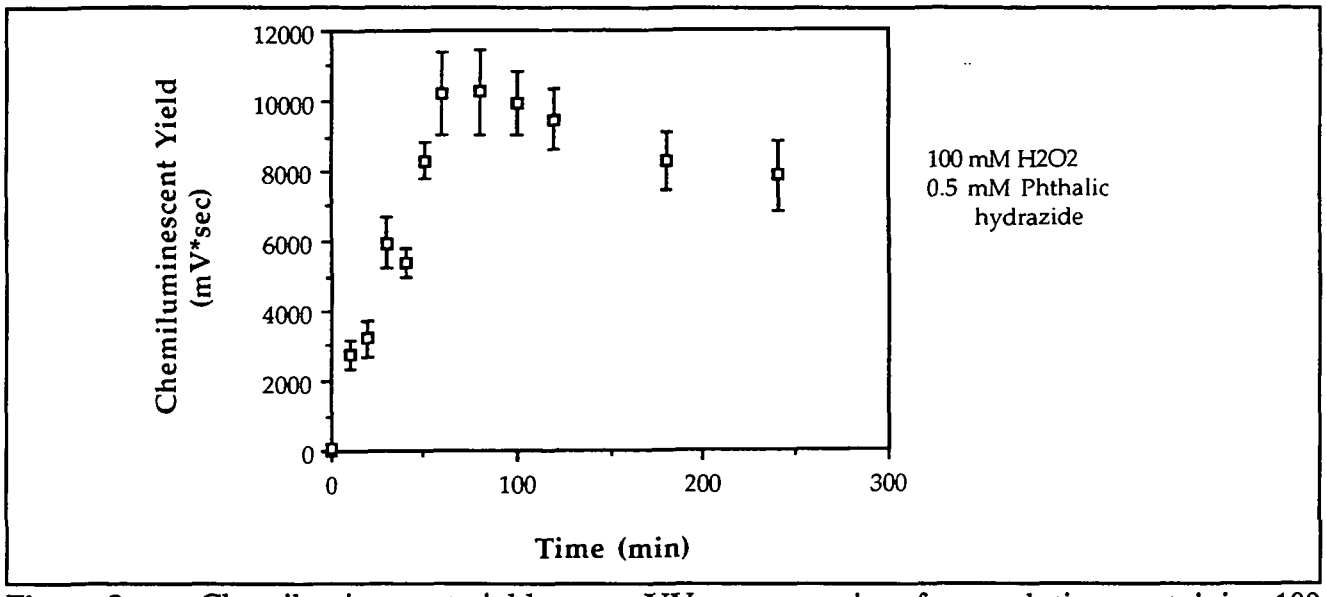


Figure 2 Chemiluminescent yield versus UV exposure time for a solution containing 100 mM H2O2 and 0.5 mM phthalic hydrazide.

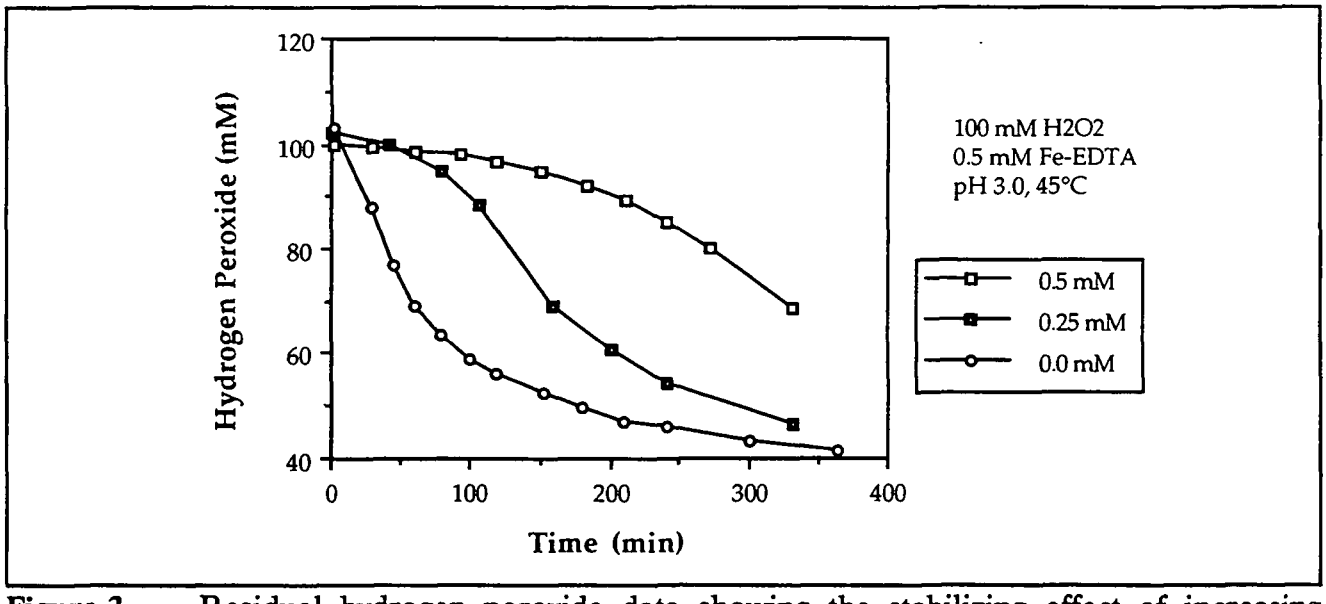


Figure 3 Residual hydrogen peroxide data showing the stabilizing effect of increasing concentrations of phthalic hydrazide.

Preliminary work with the chemiluminescence assay provide two important results, which necessitate caution when using this assay. In an attempt to overcome these limitations, a modified method for the chemiluminescence assay was developed. Phthalic hydrazide was removed from the reactor; reaction samples where then exposed to phthalic hydrazide for one minute. Results from experiments identical for those shown in Figure 3, but using the new

"external" method of the chemilluminescence assay are shown in Figure 4. The relative reaction of these systems are the same, but the chemiluminescent yields are extremely low and difficult to measure.

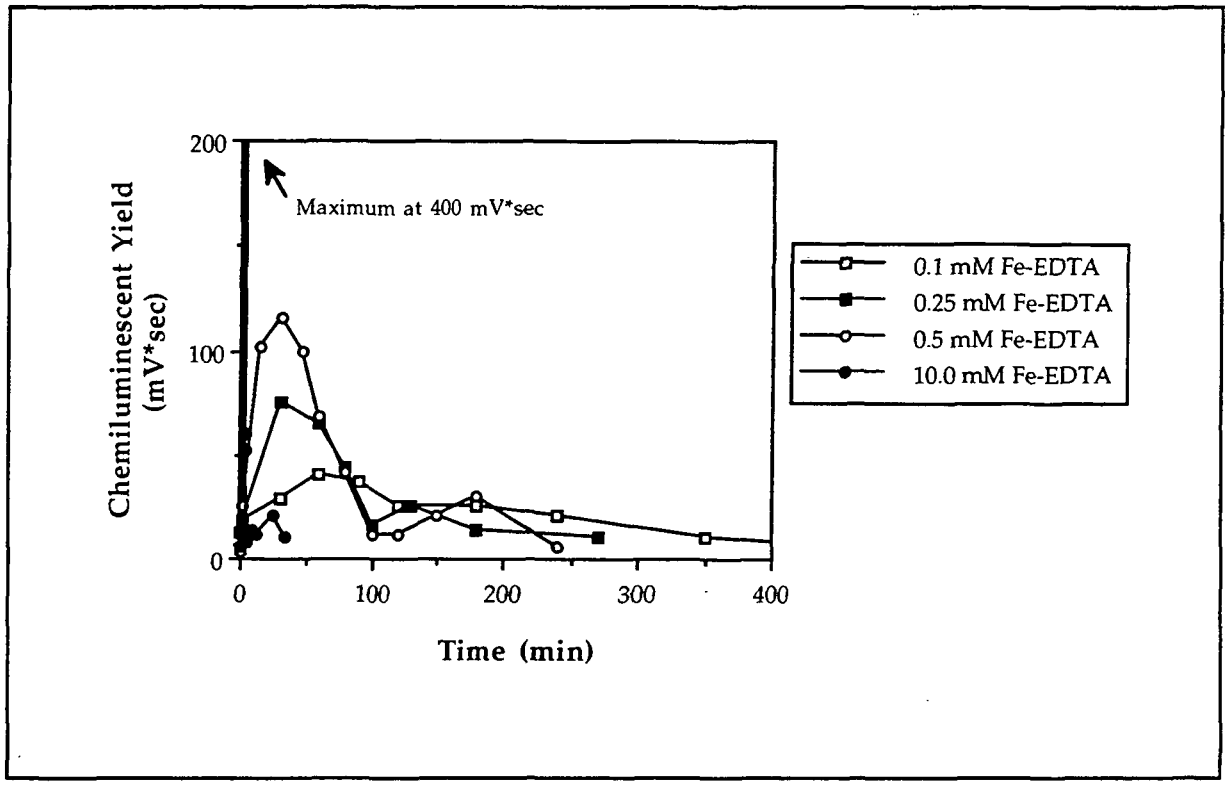


Figure 4 Chemiluminescent yields for reactions similar to those shown in Figure 1, using the external method of the chemiluminescence assay.

If the concentration of phthalic hydrazide in reaction solutions is reduced, however, the effect of phthalic hydrazide on hydrogen peroxide can be minimized. Unfortunately, this will not overcome the limitation of phthalic hydrazide degradation from excessive production of hydroxyl radicals. For systems producing large quantities of hydroxyl radicals, degradation of the phthalic hydrazide will most likely occur.

Degradation of Lignosulfonate

Reaction pH was preliminary selected at 3.0, the optimum pH for ligninase activity. 45°C was chosen as the reaction temperature. Degradation of lignosulfonate occurred in the presence of 100 mM H202 and 0.5 mM FeS04. Figure 5 shows the reduction of lignosulfonate molecular weight during reaction. The molecular weight of the lignosulfonate peak was determined by peak-position calibration of the SEC column with sulfonated polystyrene standards. During the first 20 minutes of reaction 1000 molecular weight units are lost. The degradation of the lignosulfonate shows a similar trend to the decrease in residual hydrogen peroxide concentration.

Figure 6 shows the amount of hydrogen peroxide remaining, consumed and decomposed for this reaction. Throughout the entire reaction more hydrogen peroxide is consumed by reaction with lignosulfonate than decomposed to oxygen. It is possible that some oxygen is consumed in forming iron-oxo complexes. At reaction termination 80% of reacted hydrogen peroxide was consumed while only 20% decomposed to oxygen.

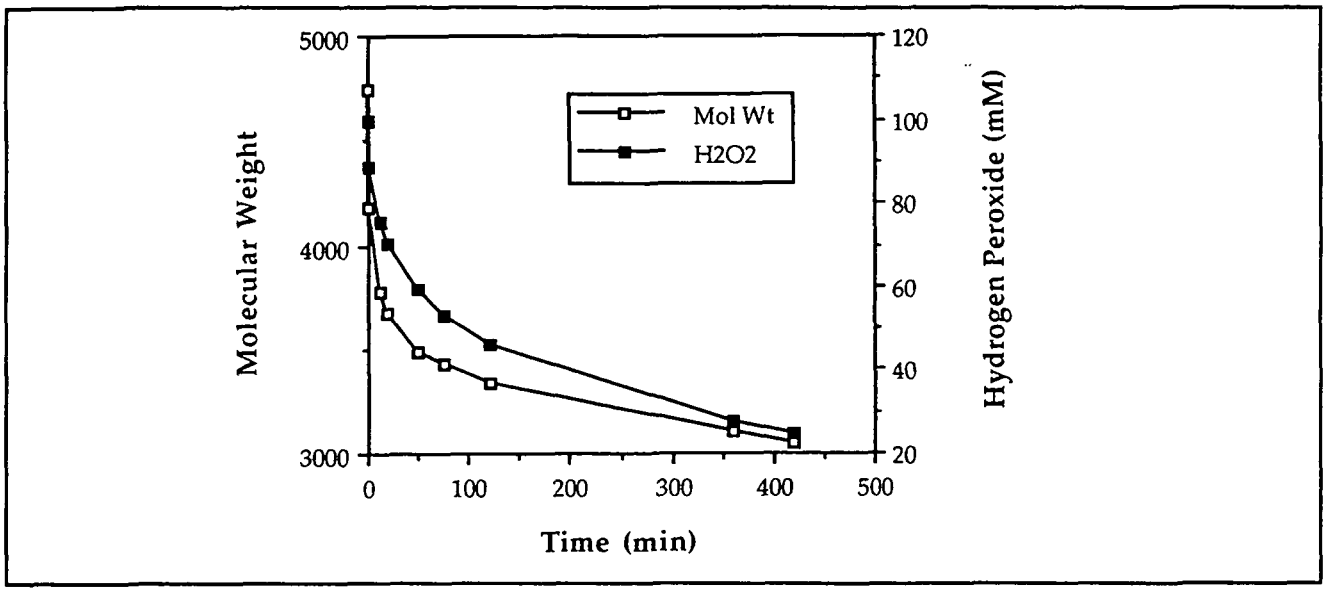


Figure 5 Molecular weight of lignosulfonate, and residual hydrogen peroxide concentration versus reaction time for 100 mM H2O2, 0.5 mM FeSO4 and 6.8 g/l lignosulfonate at pH 3.0 and 45C.

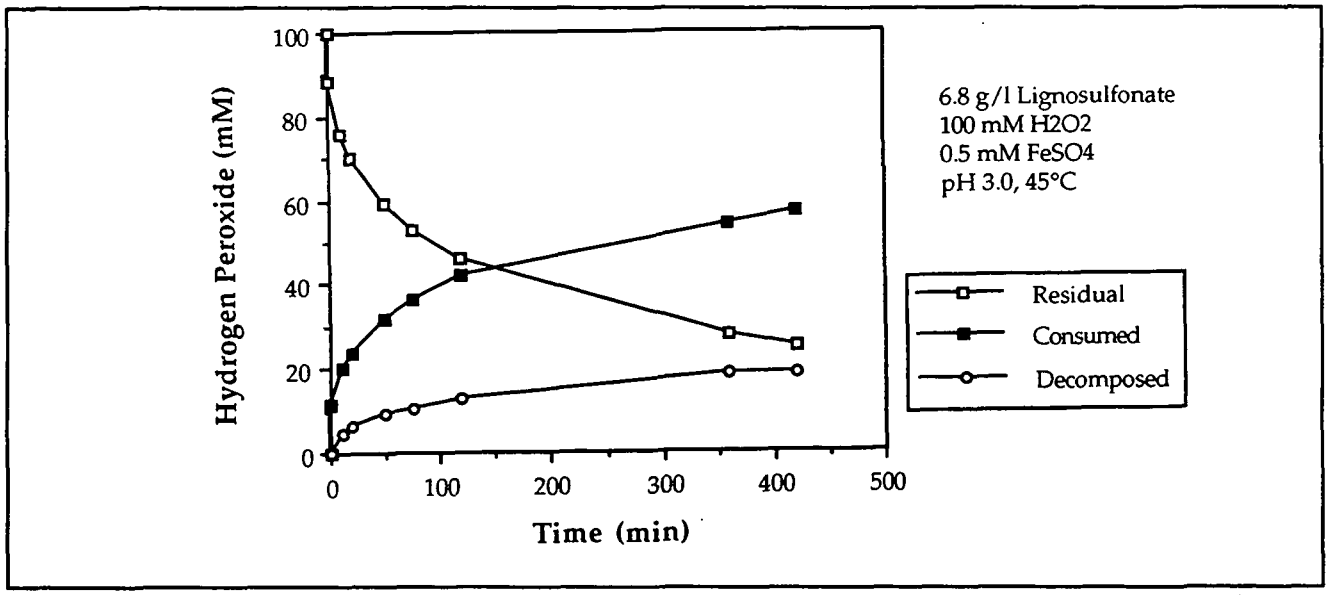


Figure 6 Residual, consumed and decomposed hydrogen peroxide for the reaction of lignosulfonate show in Figure 5.

The external method of the chemiluminescence assay was used to detect hydroxyl radicals during this experiment. Figure 7 shows the extremely low chemiluminescent yields obtained using this technique. Phthalic hydrazide must therefore be added to reaction solutions to enable detection of hydroxyl radicals produced. Such an experiment was

performed and the addition of phthalic hydrazide to the reaction drastically altered behavior in both lignosulfonate degradation and hydrogen peroxide decomposition (data not shown).

Future work will include using the chemiluminescence assay (unmodified) to detect hydroxyl radicals in the H2O2/FeSO4 system studied above using a smaller concentration (0.1 mM as opposed to 0.25 mM). Evaluation of

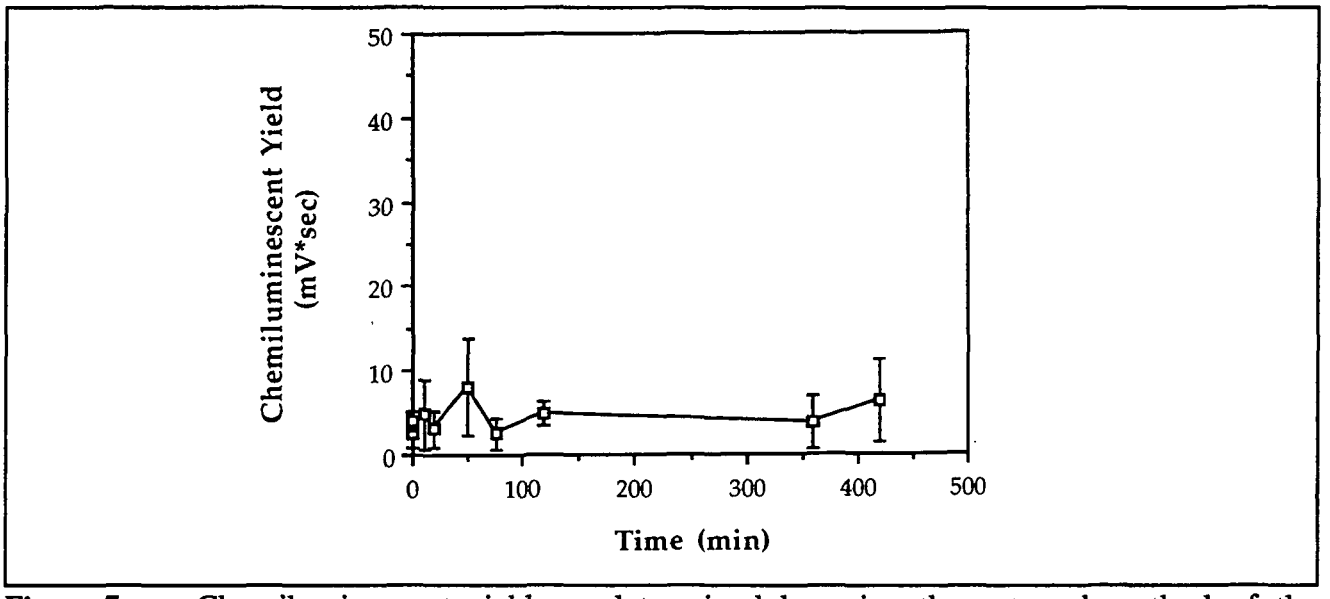


Figure 7 Chemiluminescent yield, as determined by using the external method of the chemiluminescence assay, versus reaction time for the lignosulfonate degradation shown in Figure 5.

Fe(II)-EDTA and hematin under similar conditions will then be performed and compared to the FeSO4 catalyzed system. A kinetic model for degradation of lignosulfonate under these conditions is in the process of being developed.

Degradation of Hydroxyethyl Cellulose (HEC)

For commercial bleaching of pulp with hydrogen peroxide, the ratio of cellulose to hydrogen peroxide is approximately 60:1. Several limitations of the developed experimental system prohibit using such a ratio. The viscosity of HEC solutions above 3.0 g/l results in difficult handling of the solution (a high molecular weight HEC sample is being used -- Mv of 1,000,000). A minimal H2O2 concentration of 10 mM is needed to ensure adequate measurement of hydrogen peroxide decomposed to oxygen.

A series of experiments were first performed to identify suitable reaction conditions observing these constraints. 20 mM H2O2 and 3.0 g/l HEC were found to give optimum results, although providing a cellulose:H2O2 ratio of 4.5:1.

Experiments were then performed in which two biomimetic compounds, FeSO4 and Fe(II)-EDTA, were evaluated for their effect on HEC at the selected conditions. Figure 8 shows the reduction in viscosity average molecular weight during these reactions. These molecular weights were determined by measuring the intrinsic viscosity of reaction samples and then applying the Mark-Houwink relationship. The H2O2/FeSO4 system degraded the HEC more severely than the H2O2/Fe(II)-EDTA system.

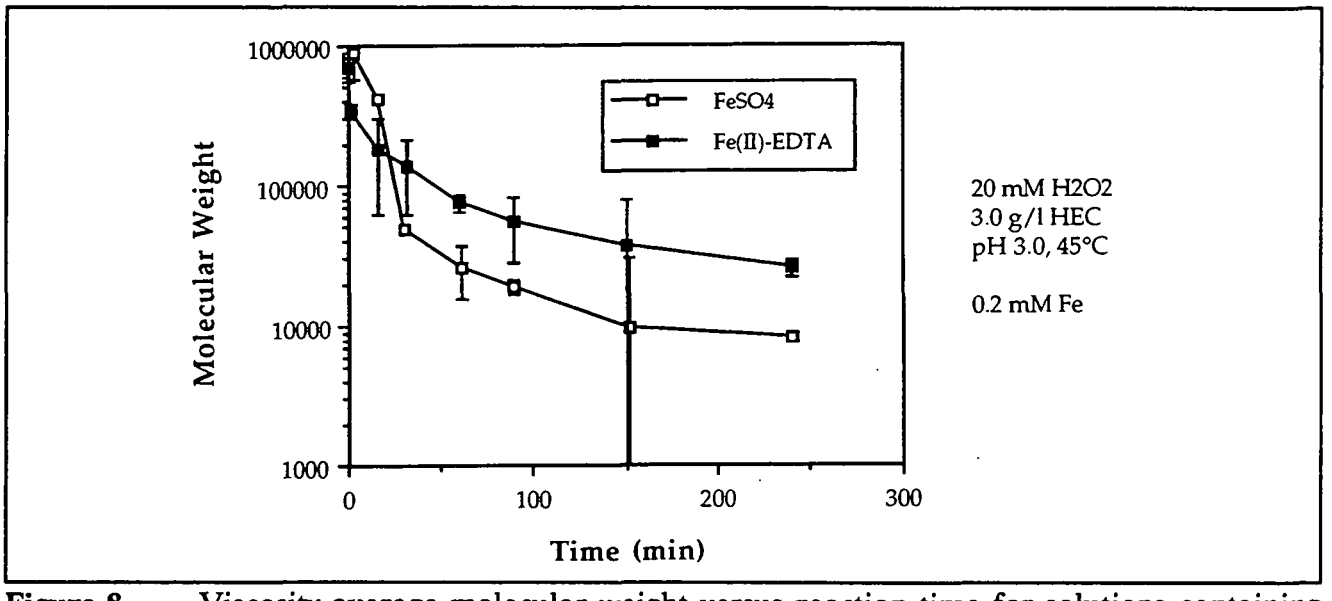


Figure 8 Viscosity average molecular weight versus reaction time for solutions containing 20 mM H2O2 and 0.2 mM of either FeSO4 or Fe(II)-EDTA.

Figure 9 shows the residual hydrogen peroxide concentration data for both of these experiments. The H2O2/FeSO4 system is much more reactive, as evidenced by grater consumption of hydrogen peroxide. During both of these reactions, no oxygen evolution was detected; therefor it could be concluded that all H2O2 was consumed by reaction. For these conditions, however, approximately 2 mM of H2O2 as oxygen is soluble in the reaction solution. Consequently, it is most likely that some H2O2 did decompose, but it was less than 2 mM.

Experiments identical to those above were performed using the chemiluminescence assay. Figure 10 shows the chemiluminescent yields from these two reactions. The H2O2/FeSO4 system generated significantly more hydroxyl radicals than the Fe(II)-EDTA catalyzed system. For the H2O2/FeSO4 system, full hydroxylation of phthalic hydrazide appears to have occurred by 125 minutes, as evidenced by the leveling off of the chemiluminescent yield curve. Degradation of the phthalic hydrazide may be occurring at 250 minutes.

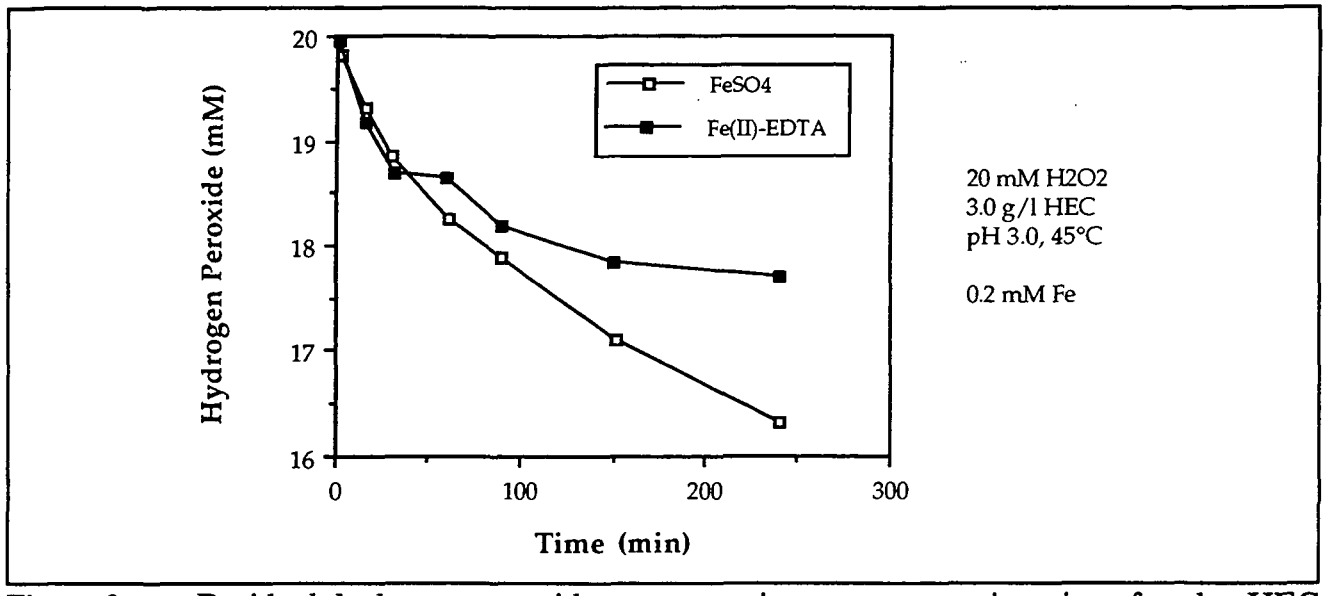


Figure 9 Residual hydrogen peroxide concentration versus reaction time for the HEC degradations show in Figure 8.

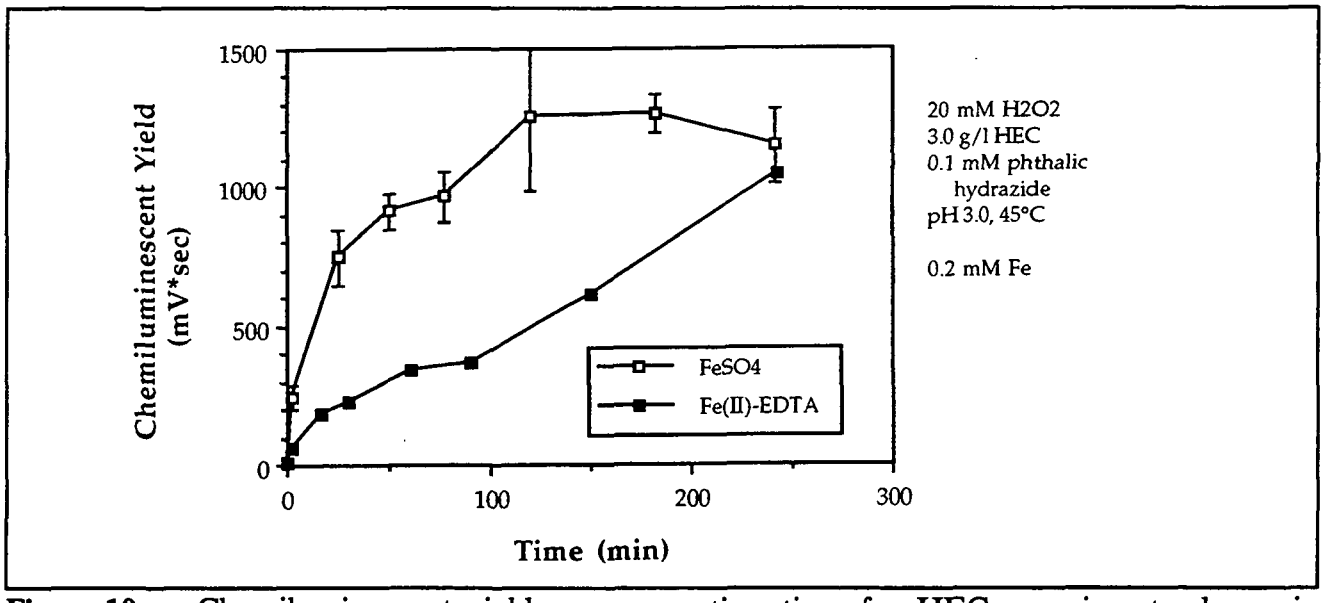


Figure 10 Chemiluminescent yield versus reaction time for HEC experiments shown in Figure 8.

For the H2O2/Fe(II)-EDTA system, complete hydroxylation of phthalic hydrazide is not achieved. Close inspection of the chemiluminescent yield curve indicates that at about 100 minutes the reaction mechanism changed as the trend becomes more linear.

For these reactions it is important to know whether the reaction has been altered by the presence of the phthalic hydrazide. Comparison of hydrogen peroxide data for the reactions with and without phthalic hydrazide for the H2O2 system indicate a minor effect. For the H2O2/Fe(II)-EDTA system, the reactions are similar for the first 75 minutes, after which the presence of the phthalic hydrazide inhibits the decomposition of hydrogen peroxide.

FUTURE WORK

Work is in progress to examine effects of Fe(II)-EDTA on lignosulfonate degradation. Once this portion is complete, the effect of hematin will then be examined. The effect of hematin on HEC degradation will also be completed. These results will then all be compared to determine which system is the most selective for lignosulfonate degradation.

The next segment of the thesis will be to modify the biomimetic compound which shows the most affinity for lignin. This modification will attempt to direct the biomimetic compound to closer proximity to the lignin component of interest. The effect of pH on reaction conditions will then be explored to find optimum efficiency. The final phase of this project will be to optimize reaction conditions for biomimetic bleaching of a softwood kraft pulp.

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SECTION 2

A FUNDAMENTAL CHARACTERIZATION OF PULP BLEACHING EFFLUENTS PRODUCED UNDER VARIOUS LOW AOX PROCESS CONDITIONS

Todd Schwantes
A-490 Thesis Research

INTRODUCTION

Environmental concern by the public, the threat of government regulation of AOX, and market pressures have led many pulp mills to implement AOX reduction strategies, including oxygen delignification, ClO_2 substitution, and oxidative extraction. Although AOX is reduced by these strategies, it remains uncertain how they actually change the character of the effluent, and its effects on the environment.

It is the goal of this thesis research to characterize bleaching effluents from low AOX processes. This characterization, along with certain already developed relationships will yield information regarding the relative potential for environmental effects among the low AOX processes studied. Information from the literature regarding the characterization will be given in later sections.

PULP BLEACHING

To date, two bleaching sequences have been studied. Both 100% ClO_2 and 100% Cl_2 lab bleaching of an oxygen bleached softwood kraft pulp have been done. Oxidative extraction (E_o) followed the D or C stage (referred to throughout this report as DC stages), in all cases. Table I shows the identification code of each effluent that had been characterized, and describes the effluent type. These codes will be used to identify effluents in the graphs of this report.

EFFLUENT CHARACTERIZATION

The effluents from both DC and E_1 stages were individually characterized by the fractionation shown in scheme I. An ether extraction of the effluent is performed, yielding two ether phases and an aqueous phase. The first ether phase (that material easily extracted by ether) is fractionated into acids, phenolics, and neutrals. Each fraction is then evaporated (repesented by dashed horizontal lines in the scheme) to remove the ether. The final result is the fractions listed in the right hand column of the scheme. A sample of the whole effluent is similarly evaporated and volatiles are determined by difference. The types of effluent fractions and the abbreviations for them, are summarized in Table II.

TOC AND AOX BALANCES:

Figures 1 and 2 show TOC balances around the ether extraction, while figures 3 and 4 show the corresponding AOX balances. Upon viewing this data, certain trends become immediately clear. Although the TOC present in the different effluent types is similar in all cases, considerably more AOX exists in the 100% Cl_2 versus 100% ClO_2 effluents and in the DC stage versus the E_1 stage effluents. It is also clear that much more ether extractable AOX is present in the 100% Cl_2 effluents.

Figures 5 and 6 show TOC balances around the fractionation of NVEE I, while figures 7 and 8 show corresponding AOX balances. It is again clear from these graphs that much more AOX is extractable by ether when 100% Cl_2 is used. These graphs also show that much more of the ether extract consists of phenolics in the case of 100% Cl_2. Although 100% ClO_2 does produce some phenolic AOX, on the scale of these graphs is does not even show up.

DATA INTERPRETATION AND DISCUSSION:

Rather than considering all fractions in detail, I've chosen to consider certain fractions based on their potential for negative environmental effects. The ether extract contains mutagenic compounds;[1,2] in fact one study found about 75% of the effluent mutagenicity was present in a 48 hour ether extract of 3L of effluent.[3] In another study the ether extract contained 92% of the C stage toxicity and 75% of the E stage toxicity.[4] The ether extracts also had number average molecular weights between 200 and 300, as determined by vapor pressure osmometry.[4] There have been claimed relationships between low molecular weight AOX and chronic and acute toxicity presented in the literature as well.[5] For these reasons it is important to consider the ether extract; both ether phases will be considered since the effect of extraction time on environmental parameters is unclear. We would expect the NVEE II phase to be less of an environmental threat since it must be more polar and/or of higher molecular weight than NVEE I.

Within the NVEE I phase, NVEEP and NVEEN are likely to be of the most interest environmentally, since they are the most non-polar and the most likely bio-available materials. Although the phenolic and neutral fractions were found in only small amounts in a previous study, they were however, highly toxic.[4] The following fractions will be considered in

some detail: NVEE I, NVEE II, NVEEP, and NVEEN. The whole effluent will be considered as a base case.

TOC And AOX In Effluent Fractions:

Figures 9 and 10 show the TOC and AOX in each of the whole effluents. It is again clear that AOX is higher in the 100% Cl_2 effluents versus 100% ClO_2, and in the DC stages versus the E_o stages.

Figures 11 and 12 show the TOC and AOX of each NVEE I fraction. The trends are again similar but more pronounced. In the case of a 100% Cl_2 DC stage, the carbon and chlorine are present in approximately the same amounts by weight. This is the first time a large inconsistency appears in the data; $E_1$4146-61 and $E_1$4146-71 are replicates, yet the extractable TOC differs greatly. Another replicate is currently being done to see if this is just random variation or if a problem occurred during bleaching or fractionation.

Figures 13 and 14 show the TOC and AOX in each NVEE II fraction. Carbon and chlorine are generally lower in each case than in NVEE I. The data are scattered, but on the average there appears to be more AOX in the 100% Cl_2 effluents and in the DC stages.

Figures 15 and 16 show the same type of data again, but this time for NVEEP. This data is quite similar to that previously shown for NVEE I. It becomes very clear from these graphs how much more AOX is present in the phenolics from 100% Cl_2 bleaching versus 100% ClO_2 bleaching.

Figures 17 and 18 are the final graphs of this type, and show the same kind of data for NVEEN. The TOC is somewhat evenly distributed among all the effluents. The AOX is more evenly distributed and lower than most other fractions; the AOX still appears to be greater in 100% Cl_2 effluents however.

C/Cl And Percentages Of TOC Within Fractions:

The data as presented so far is interesting but difficult to understand. Since each bleaching run delignifies the pulp to different extents, comparisons based on TOC or AOX alone are not completely fair. For example, 100% ClO_2 bleached samples are not delignified as

much as with 100% Cl_2, therefore more bleaching needs to be done to reach an equal level of delignification. More TOC and AOX will be released during the additional bleaching.

The C/Cl is an objective measure, since it is based on the amount of material removed. It also may give an indication of the potential for environmental impact, since within certain classifications of material, toxicity[6,7] and lipophilicity[8] increase as the amount of chlorine per unit carbon increases (or as C/Cl decreases). Although these trends are shown within specific groups of compounds, perhaps they are also valid within the classes of this characterization.

To compare all sequences objectively, the amount of material in each fraction (as TOC) will be expressed as a percentage of the whole effluent TOC. Using this and the C/Cl, we will have a measure of how much material is present in each fraction and an estimate the fraction's potential for environmental effects. Both measures are not biased by different levels of lignin removal.

Figures 19-23 show the molar C/Cl for the whole effluent, NVEE I, NVEE II, NVEEP, and NVEEN. Figures 24-27 express the amount of material present in NVEE I, NVEE II, NVEEP, and NVEEN as a percentage of whole effluent TOC. Although interesting observations can be made from these graphs, once the data set is complete analysis of variance will be done to determine which effects are statistically significant.

The C/Cl is about 5.6 times higher for the 100% ClO_2 DC stage than for the 100% Cl_2 effluent. The C/Cl is about 6 times higher for the E_1 effluents produced from 100% ClO_2 bleaching versus the 100% Cl_2 case. Also in the case of both ClO_2 and Cl_2 bleaching, the C/Cl is about 5 times higher for the E_1 stage compared to the DC stage.

For all effluents, the C/Cl for NVEE I is lower than that of the whole effluents. This supports the contention that the fraction is of environmental significance. In the case of DC stage effluents, the 100% ClO_2 NVEE I C/Cl is about 6.8 times higher than the 100% Cl_2 case. So although a change from Cl_2 to ClO_2 produces an expected change in the whole effluent, the effect on C/Cl is greater in the portion of the effluent that is of greatest environmental concern. A change from Cl_2 to ClO_2 also seems to, on the average, reduce the percentage of the effluent TOC present in NVEE I. In the case of the E_1 stage effluents, the NVEE I C/Cl increases about 5.3 times with a change from Cl_2 to ClO_2. On the average,

there again appears to be a lower percentage of the TOC present in this fraction when 100% ClO_2 is used. The NVEE I C/Cl is 4 to 6 times higher for E_1 versus DC stage effluents.

Because of the considerable scatter in NVEE II, not many conclusions can be drawn regarding the percentages of TOC in each effluent. The E_1 stage effluents have a higher C/Cl than the corresponding DC stage effluents. Also as expected, C/Cl seems to increase when ClO_2 is used rather than Cl_2.

In the case of NVEEP, some fairly strong conclusions can again be drawn. A change from Cl_2 to ClO_2 increases the NVEEP C/Cl about 8 times for the DC stage effluents and about 4.4 times for the E_1 stages. Again it is seen that the effect of a change from Cl_2 to ClO_2 on C/Cl, is greater in the most environmentally threatening fraction--at least in the case of the DC stage. It is also clear from this data that the percentage of TOC in NVEEP is reduced when ClO_2 is used, particularly for DC effluents but perhaps in the E_1 case as well.

In the case of NVEEN, the C/Cl are higher for E_1 stage effluents than for DC stage effluents, and are higher when ClO_2 is used rather than Cl_2. Because of scatter, it is difficult to say whether differences in the percentage of NVEEN in each effluent differs.

FUTURE WORK

The next effluents prepared and analyzed will be those from 100% ClO_2 bleaching of a non-oxygen bleached softwood. This will complete the set of experiments at 30 minutes of DC stage bleaching time. Once this set of experiments is done, a second set will be started. It will consider DC stage reaction time and pH for the 100% ClO_2 bleaching of the oxygen bleached softwood pulp.

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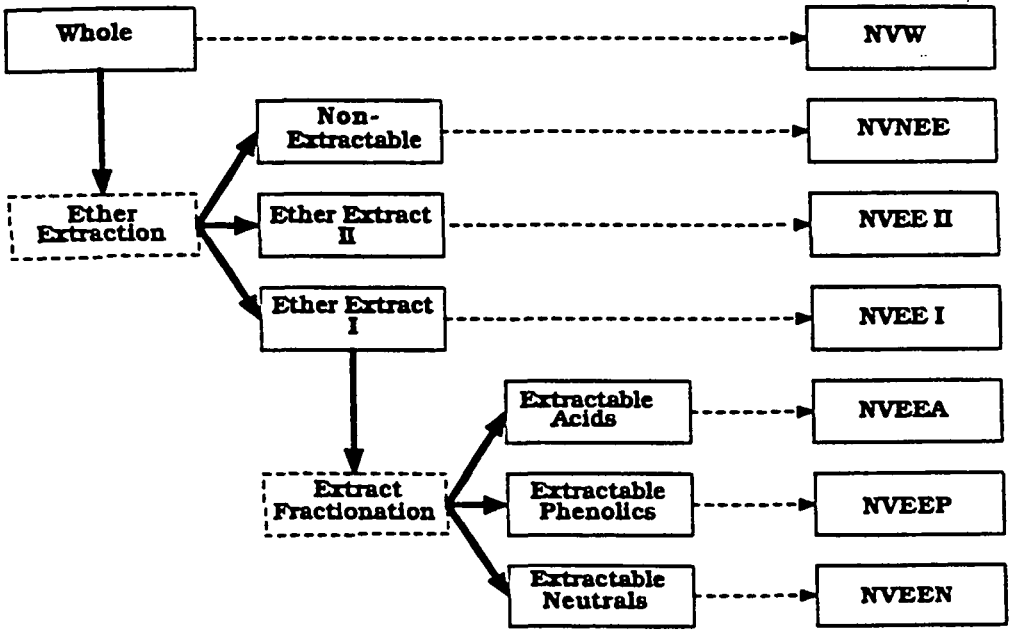
Table I: Effluent identification codes and descriptions.

Effluent	Type
DC4146-36	100% ClO_2, O_2 bleached softwood
DC4146-48	100% ClO_2, O_2 bleached softwood
DC4146-61	100% Cl_2, O_2 bleached softwood
DC4146-70	100% Cl_2, O_2 bleached softwood
$E_1$4146-36	E_o following DC4146-36
$E_1$4146-49	E_o following DC4146-48
$E_1$4246-61	E_o following DC4146-61
$E_1$4146-71	E_o following DC4146-70

Table II: Effluent fraction abbreviations and type.

Fraction	Type
NVW	non-volatile, whole
NVNEE	non-volatile, non-ether extractable
NVEE II	non-volatile, ether extractable, second phase
NVEE I	non-volatile, ether extractable, first phase
NVEEA	non-volatile, ether extractable acids
NVEEP	non-volatile, ether extractable phenolics
NVEEN	non-volatile, ether extractable neutrals



Scheme I: Effluent fractionation.

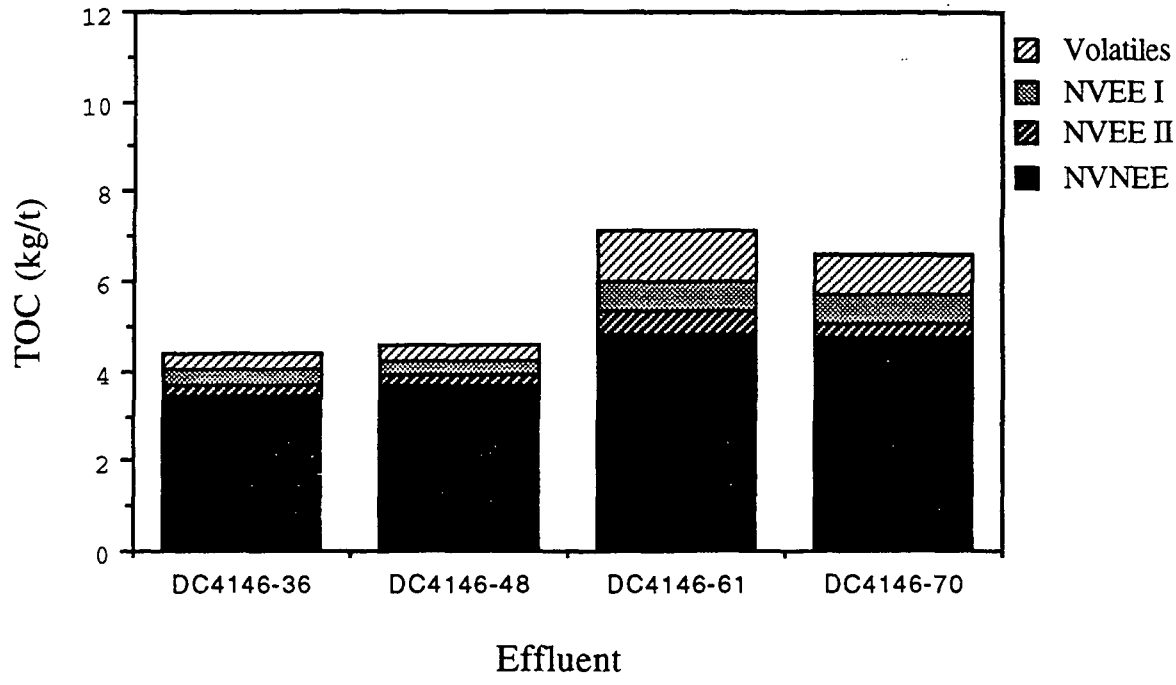


Figure 1: TOC balances around ether extraction for DC effluents.

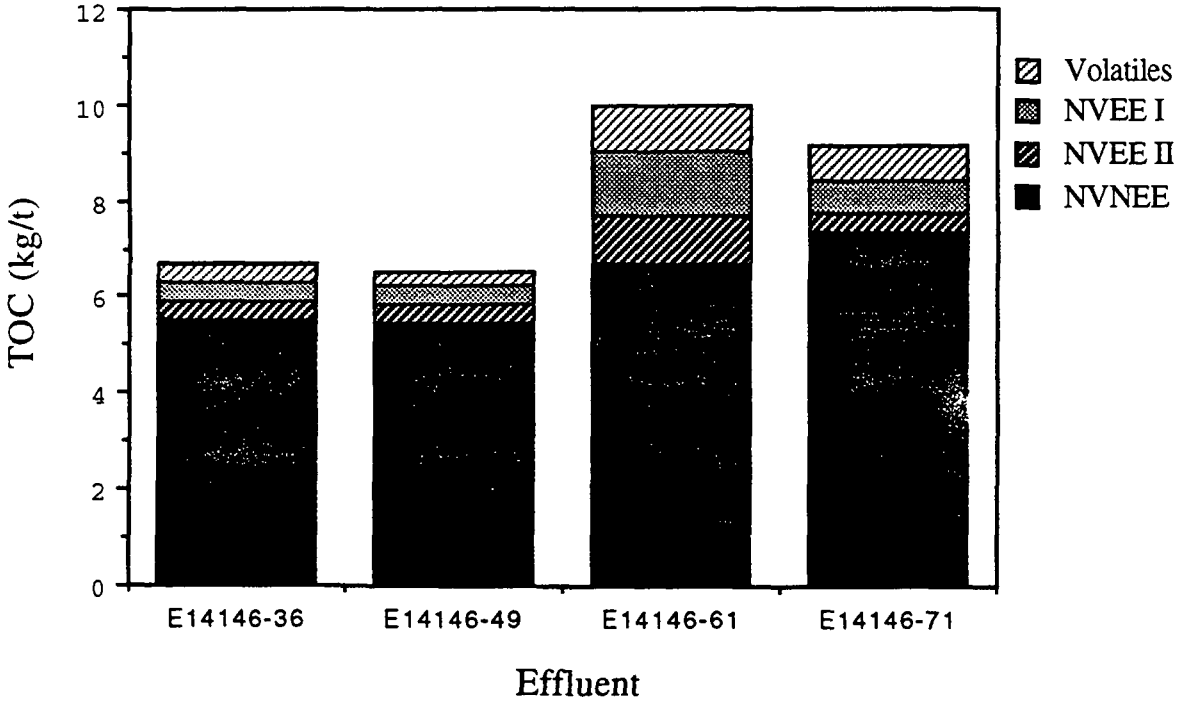


Figure 2: TOC balances around ether extraction for E_1 effluents.

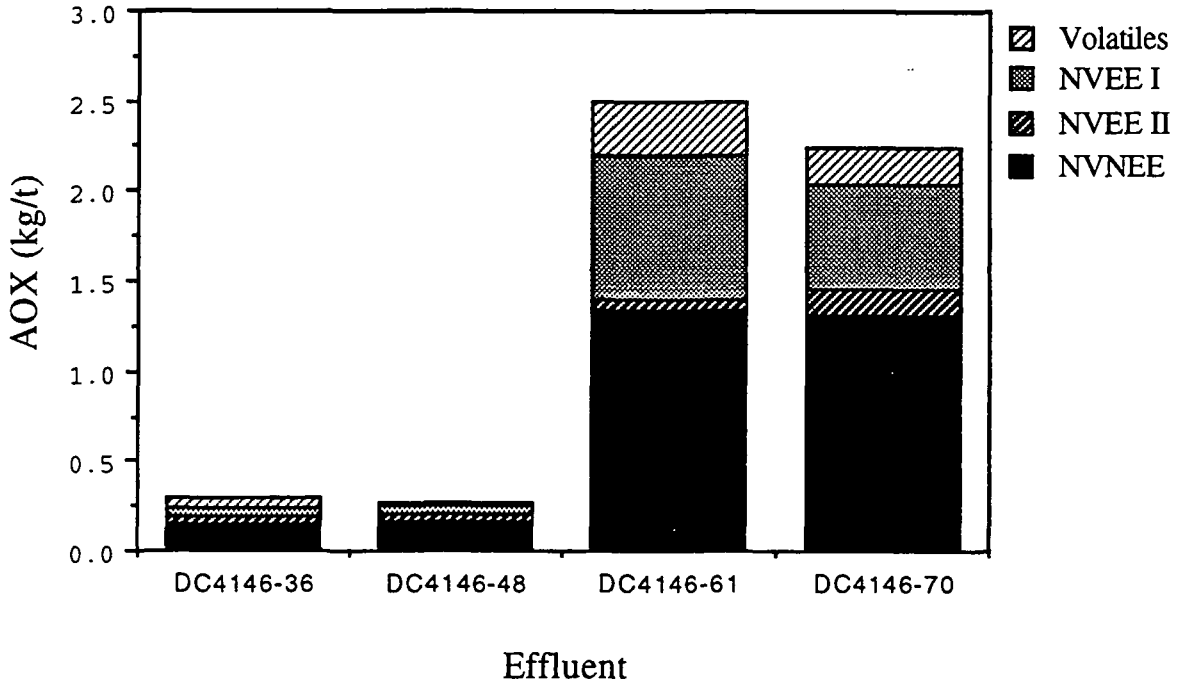


Figure 3: AOX balances around ether extraction for DC effluents.

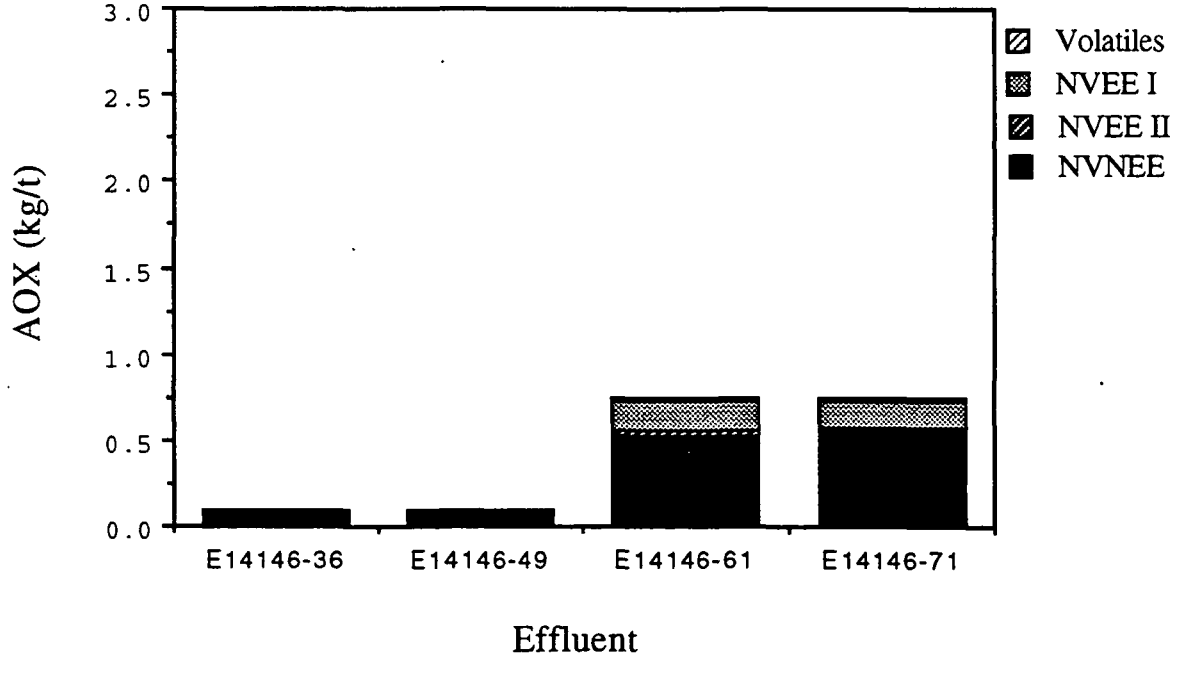


Figure 4: AOX balances around ether extraction for E_1 effluents.

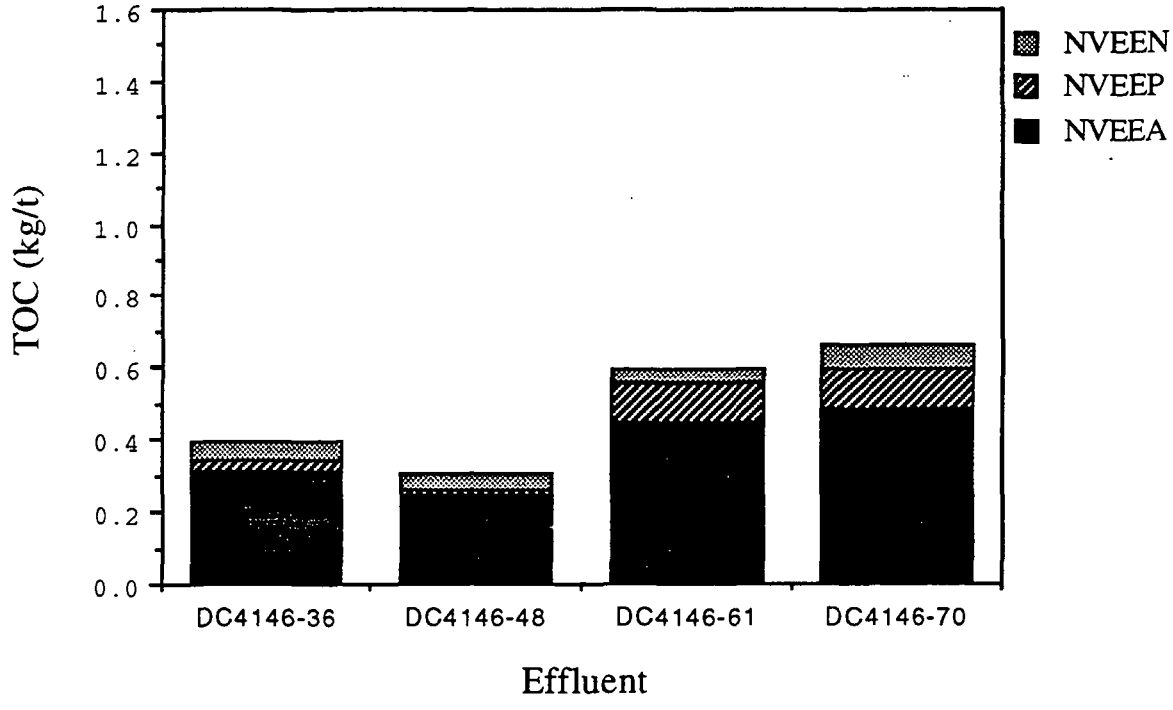


Figure 5: TOC balances around NVEE I fractionation for DC effluents.

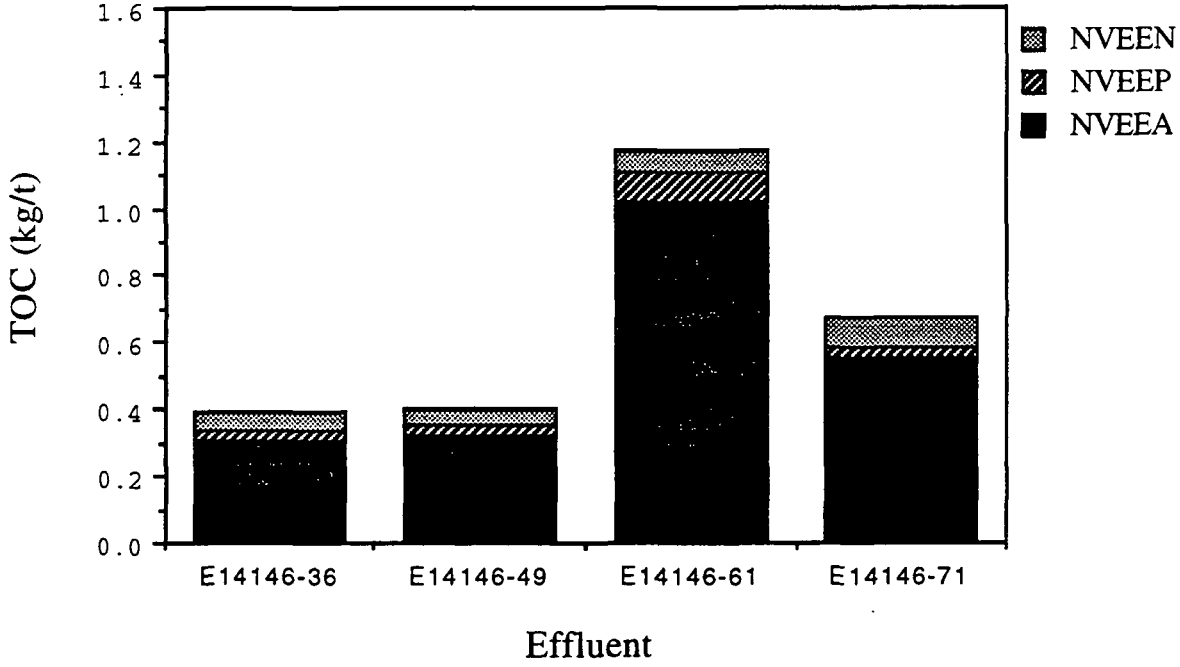


Figure 6: TOC balances around NVEE I fractionation for E_1 effluents.

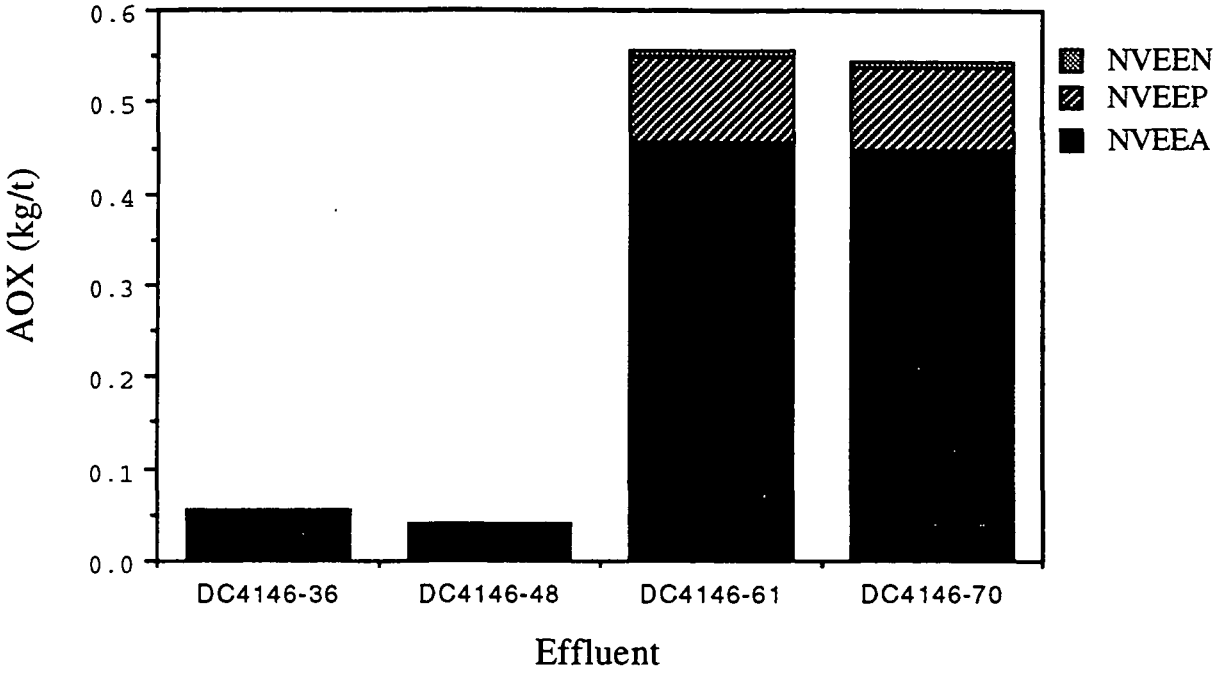


Figure 7: AOX balances around NVEE I fractionation for DC effluents.

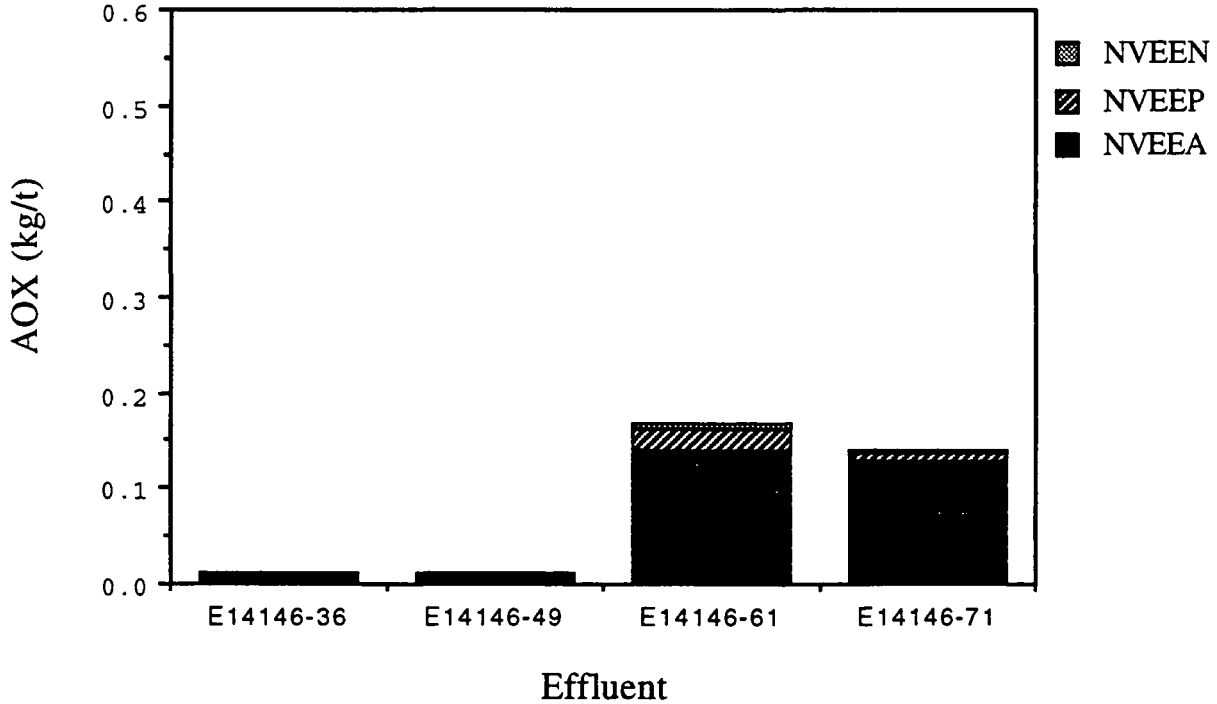


Figure 8: AOX balances around NVEE I fractionation for E_1 effluents.

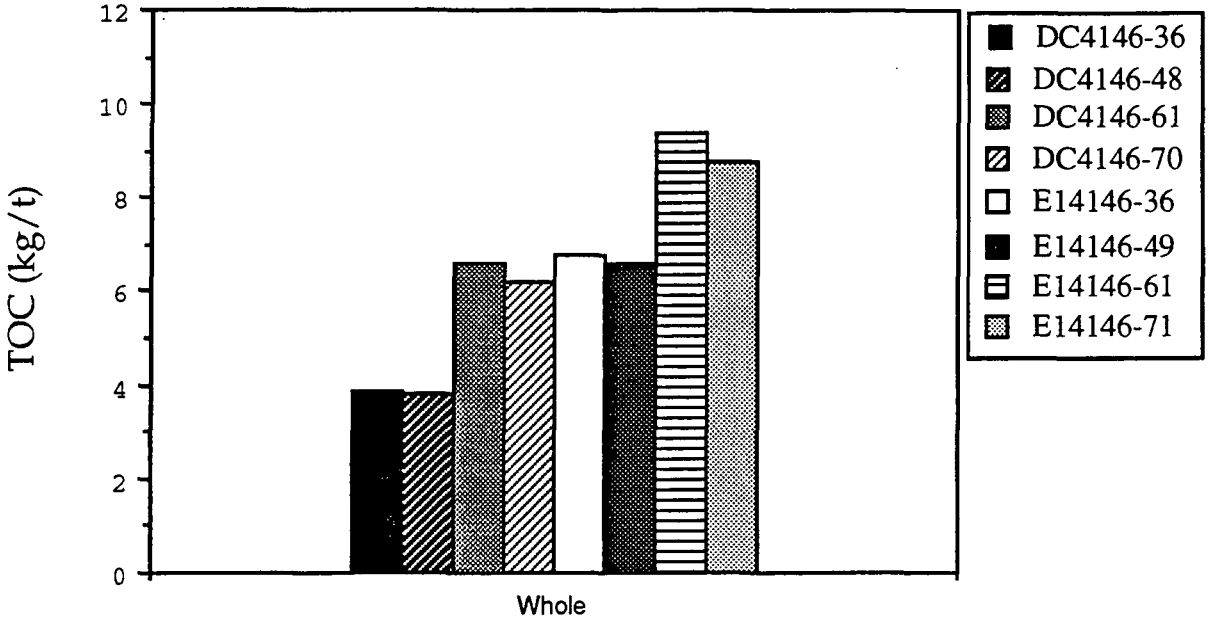


Figure 9: TOC in whole effluents.

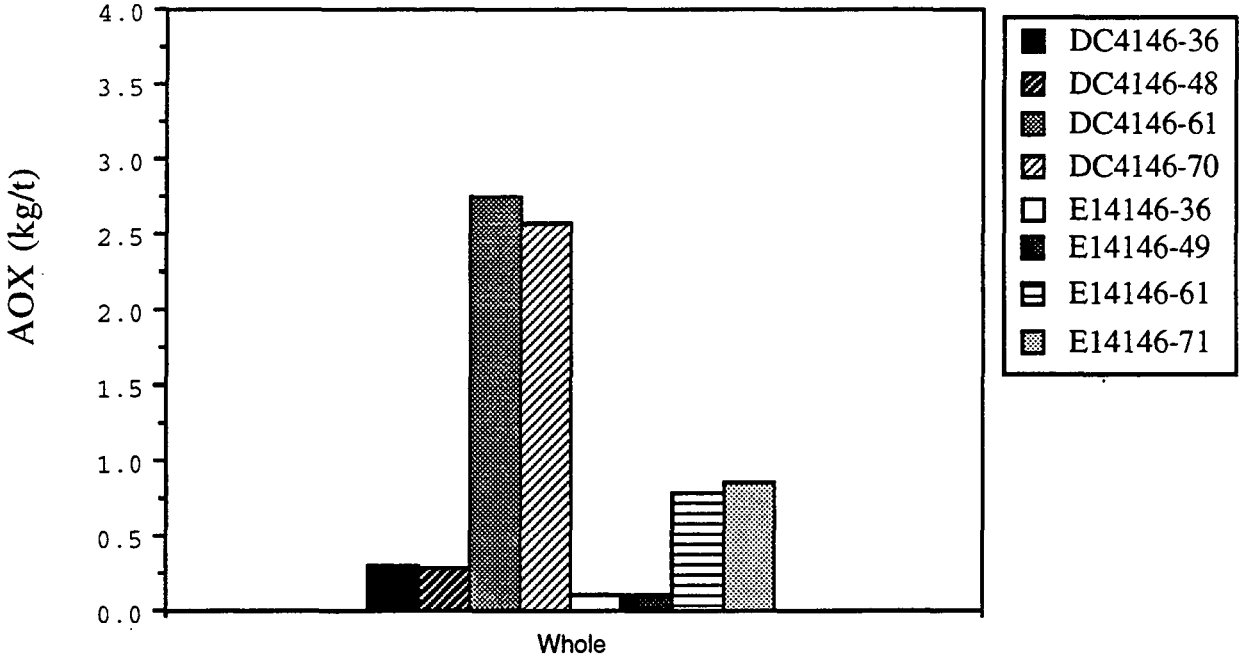


Figure 10: AOX in whole effluents.

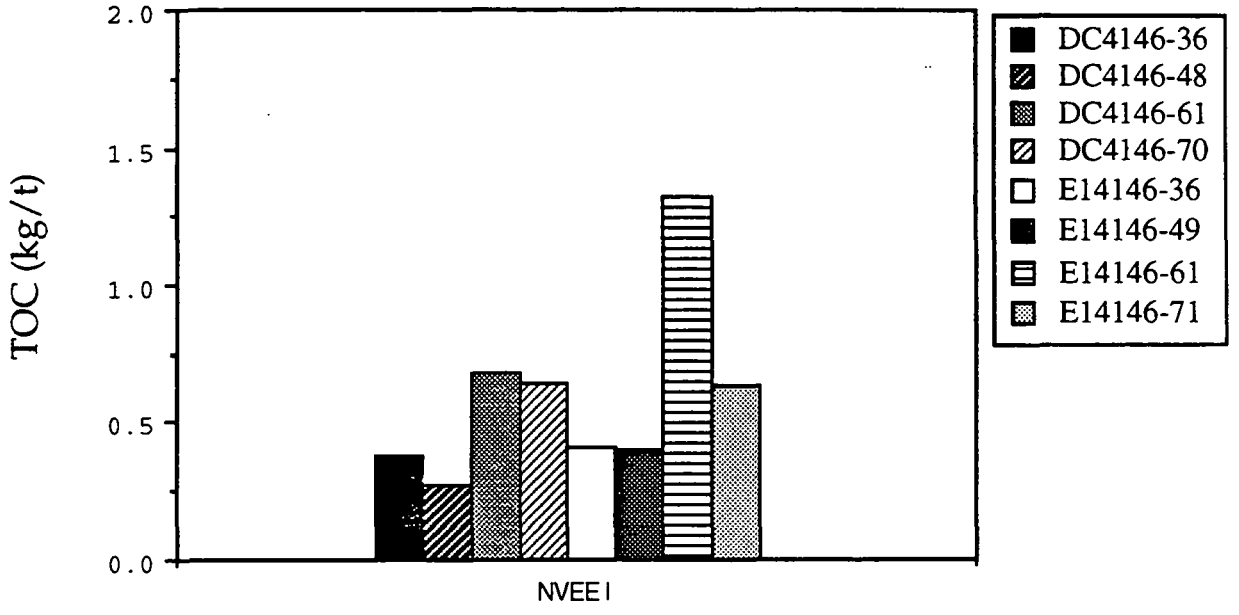


Figure 11: TOC in NVEE I.

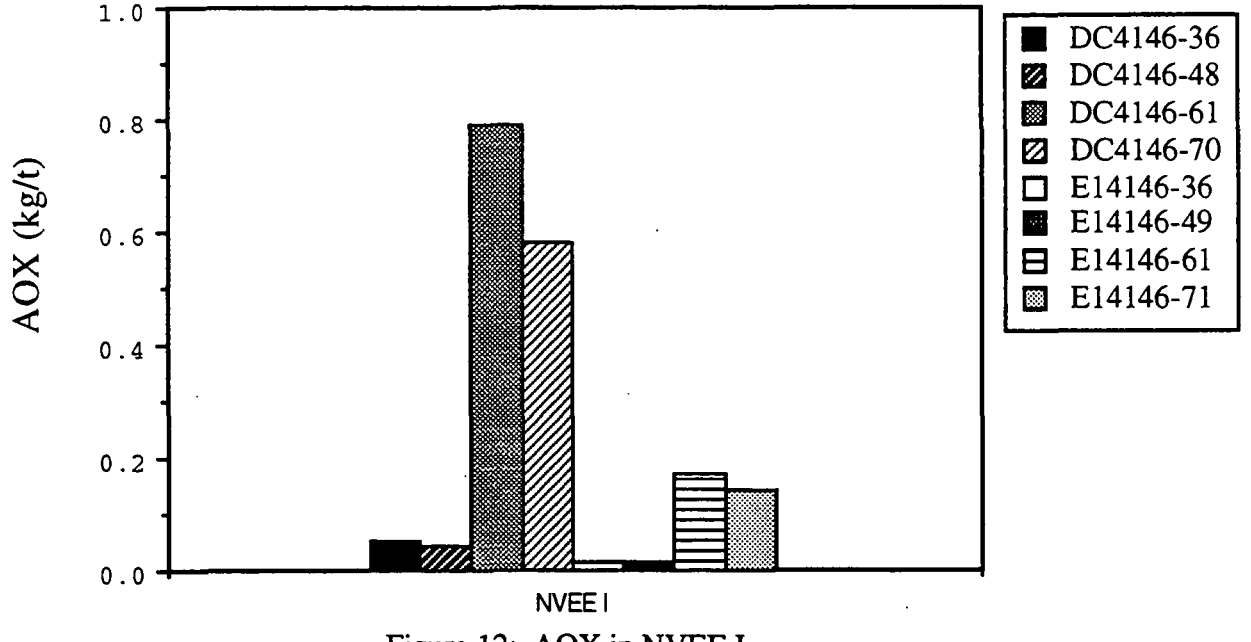


Figure 12: AOX in NVEE I.

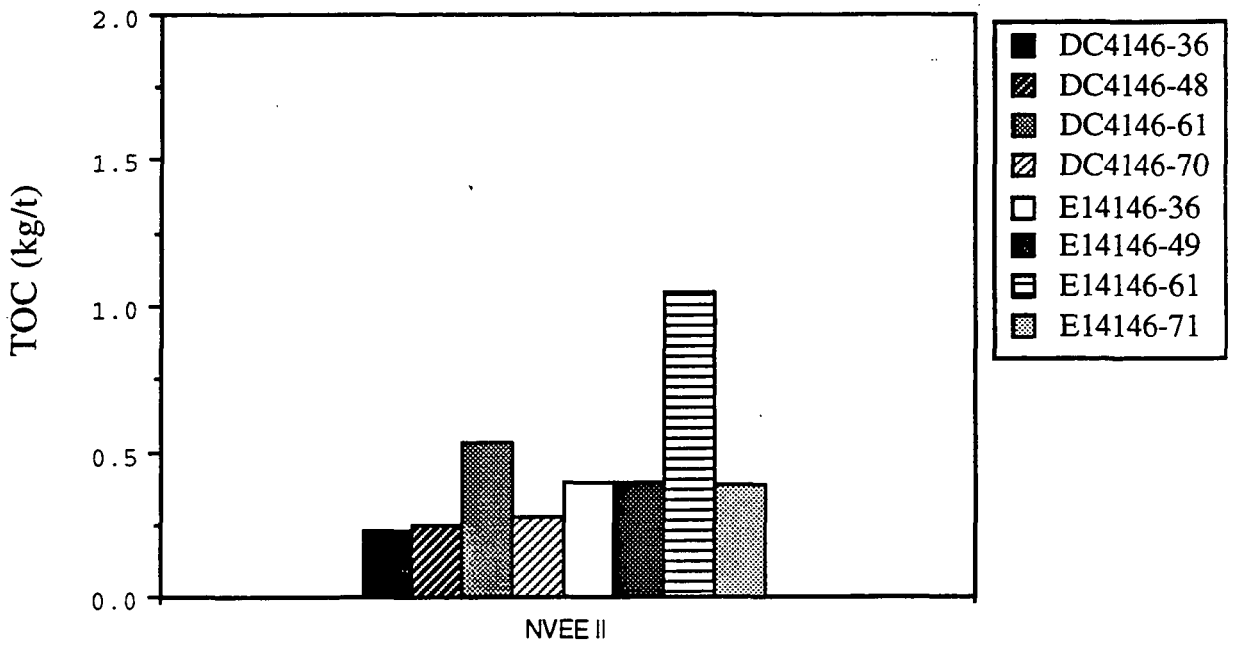


Figure 13: TOC in NVEE II.

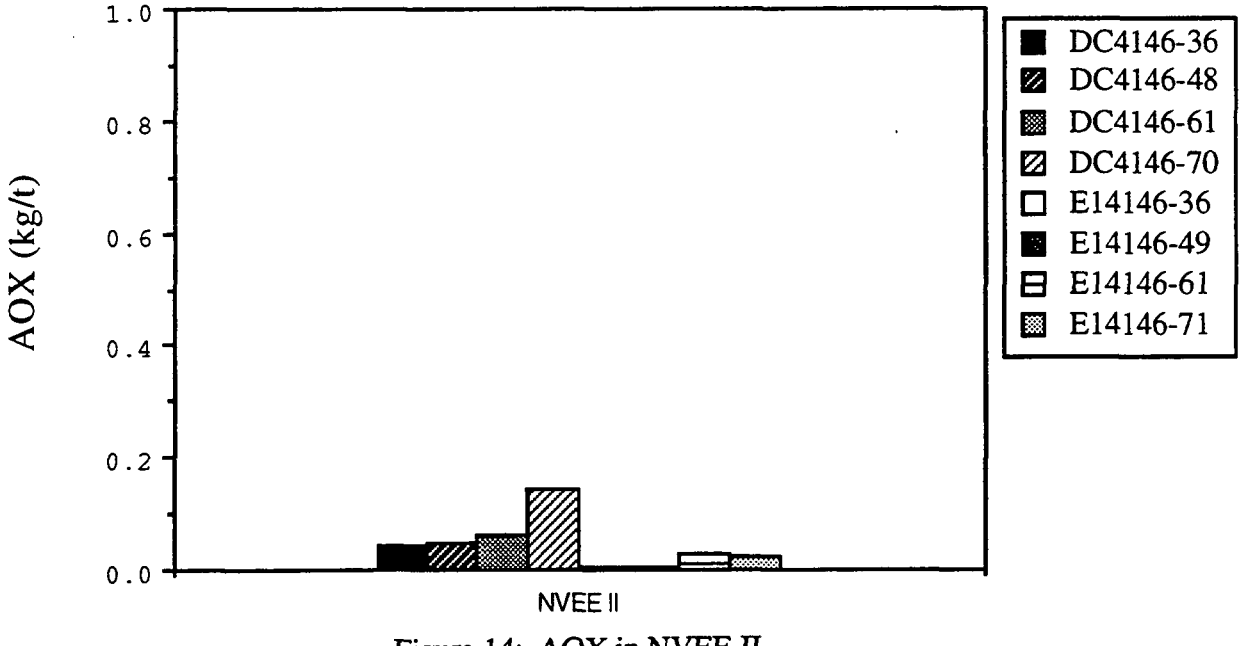


Figure 14: AOX in NVEE II.

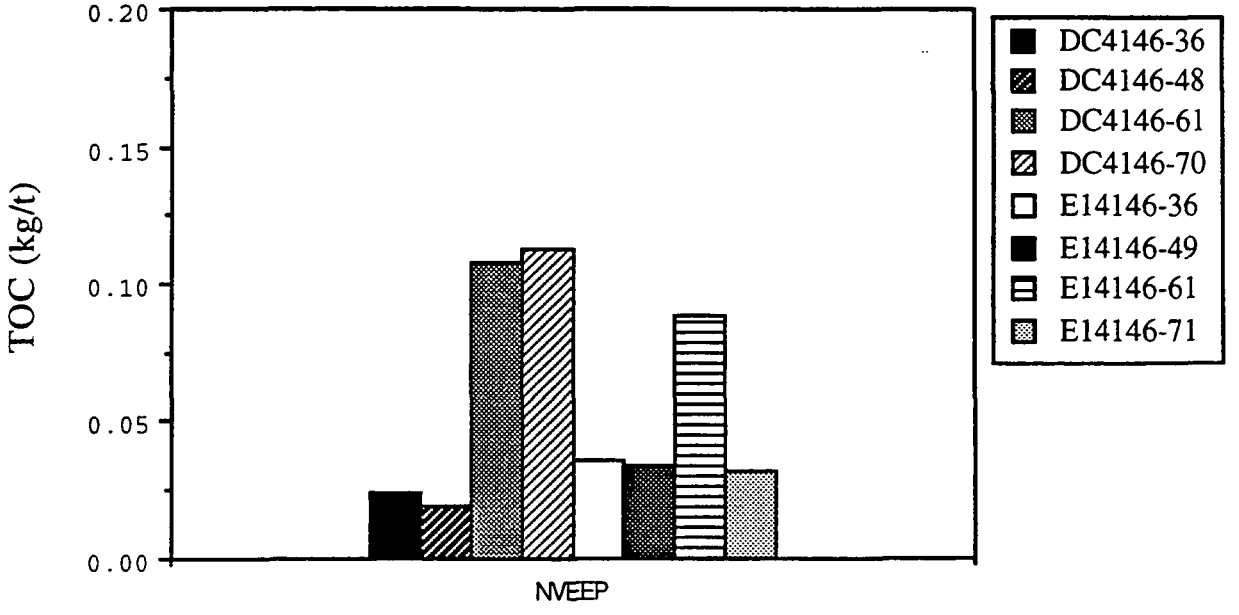


Figure 15: TOC in NVEEP.

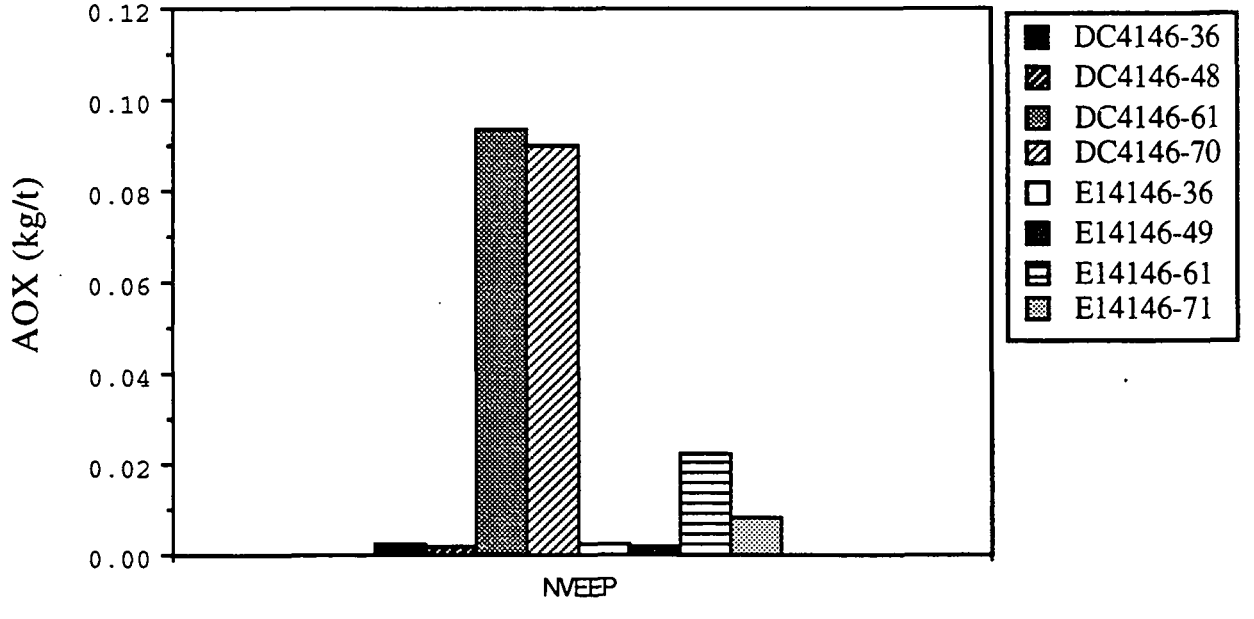


Figure 16: AOX in NVEEP.

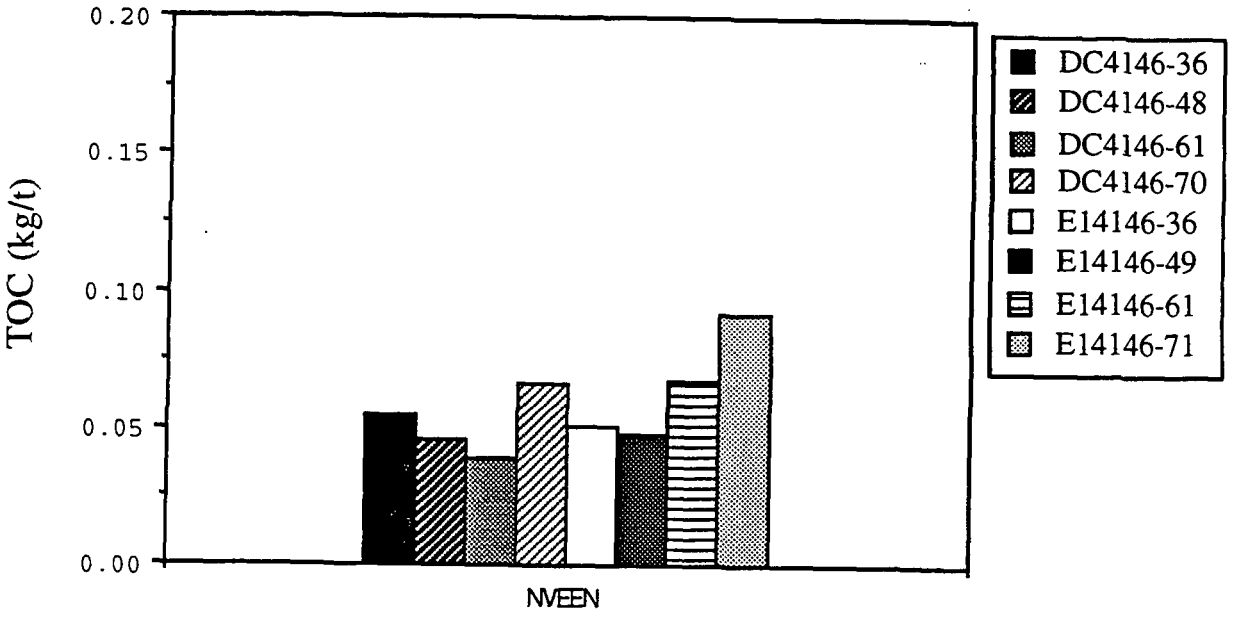


Figure 17: TOC in NVEEN.

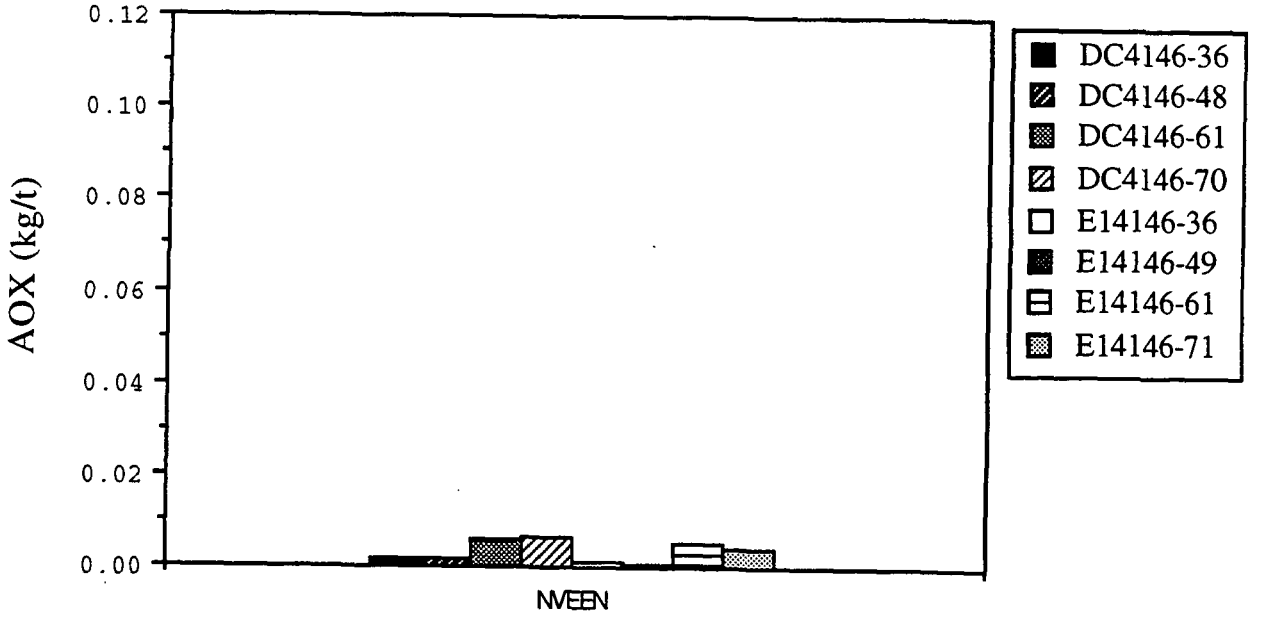


Figure 18: AOX in NVEEN.

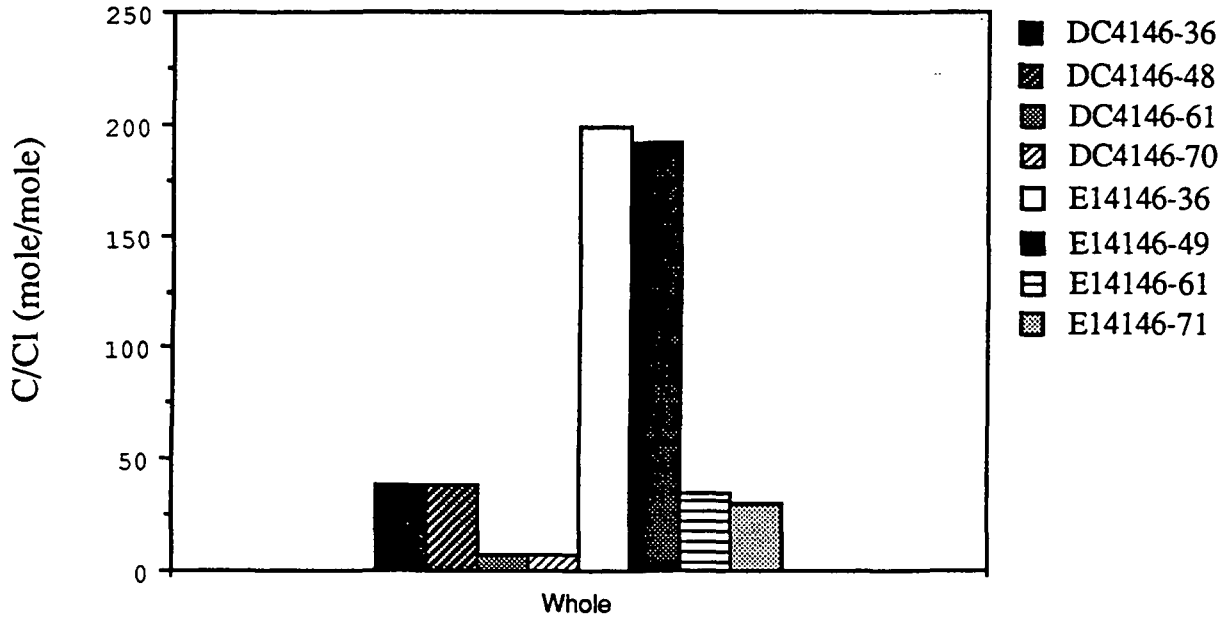


Figure 19: C/Cl for whole effluents.

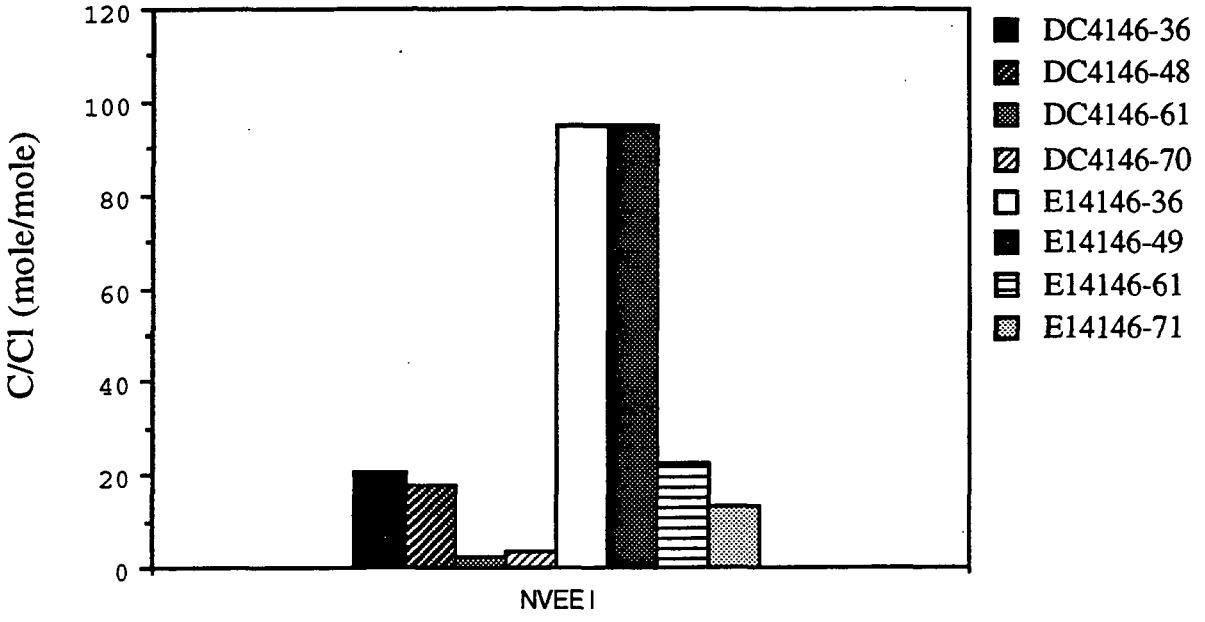


Figure 20: C/Cl for NVEE I.

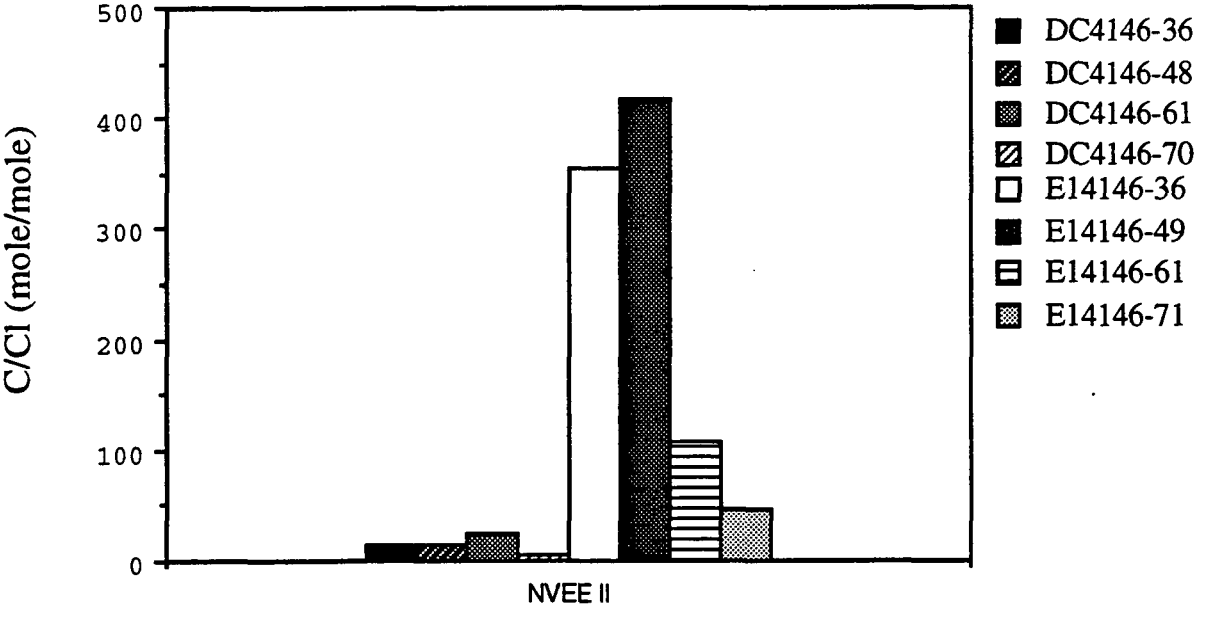


Figure 21: C/Cl for NVEE II.

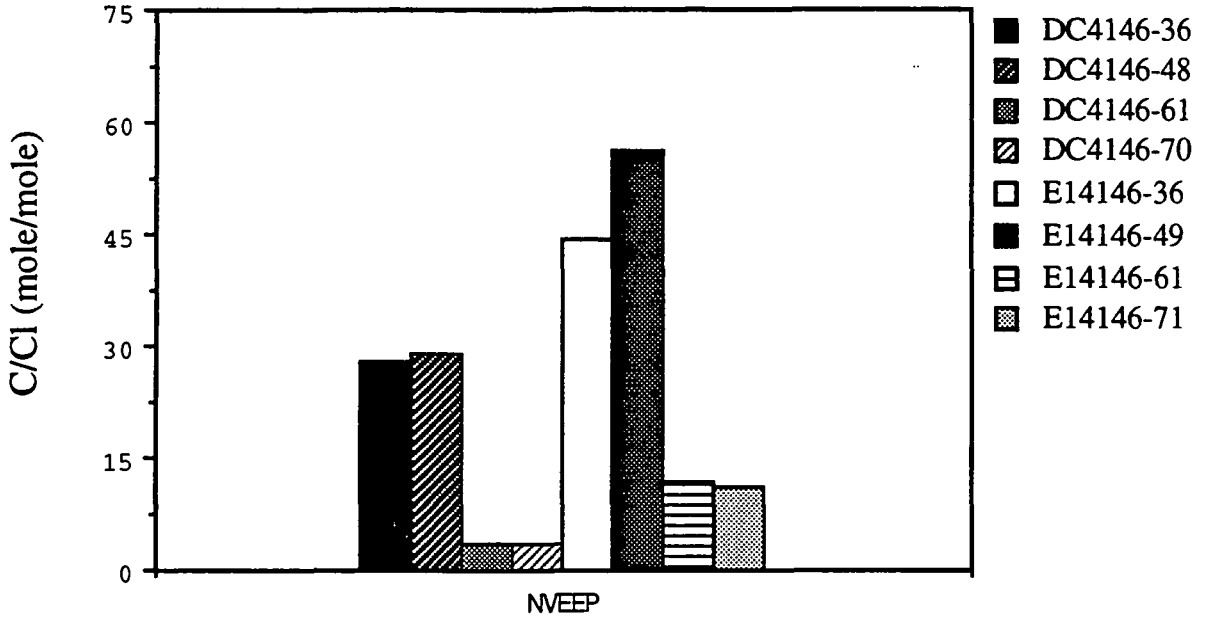


Figure 22: C/Cl for NVEEP.

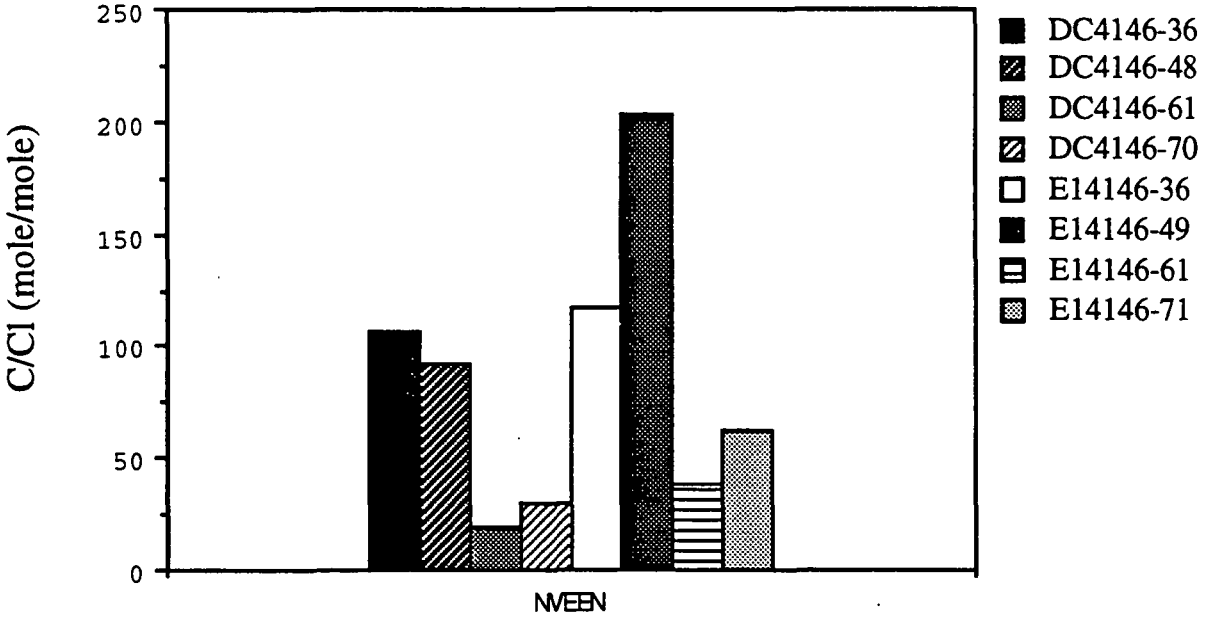


Figure 23: C/Cl for NVEEN.

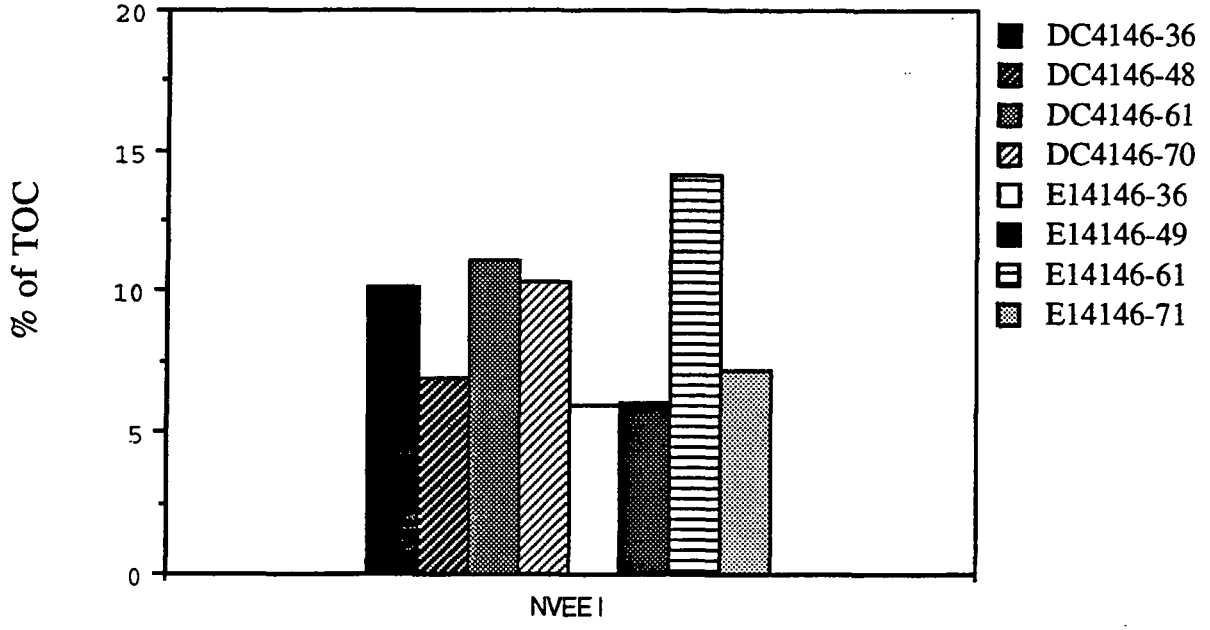


Figure 24: Percent of TOC in NVEE I.

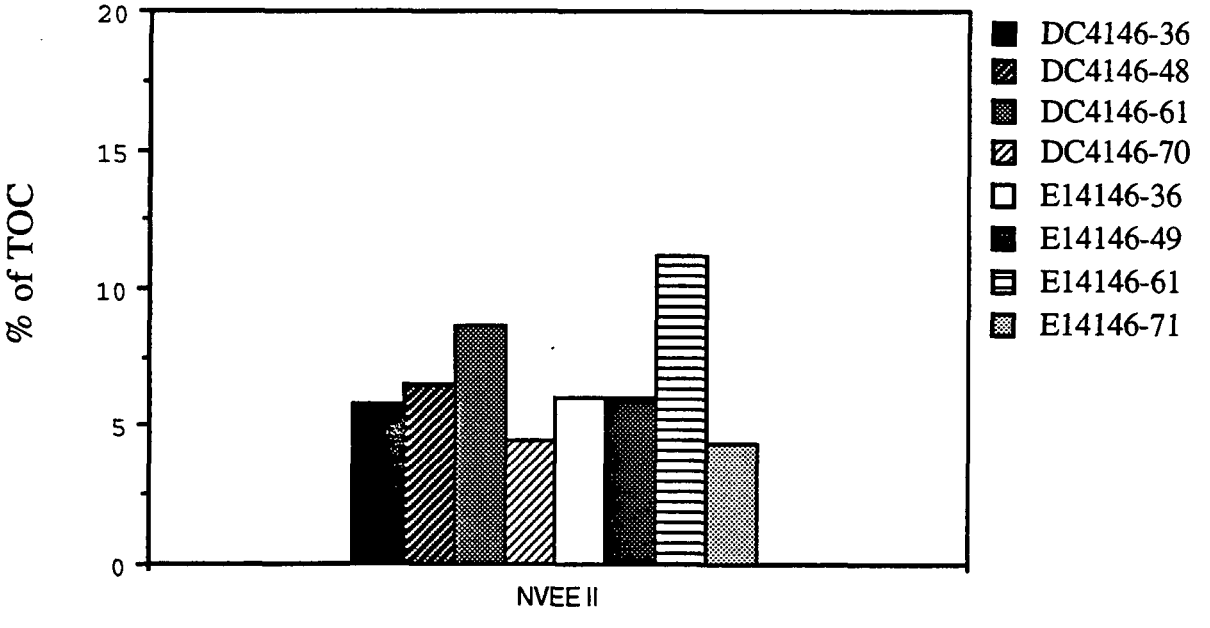


Figure 25: Percent of TOC in NVEE II.

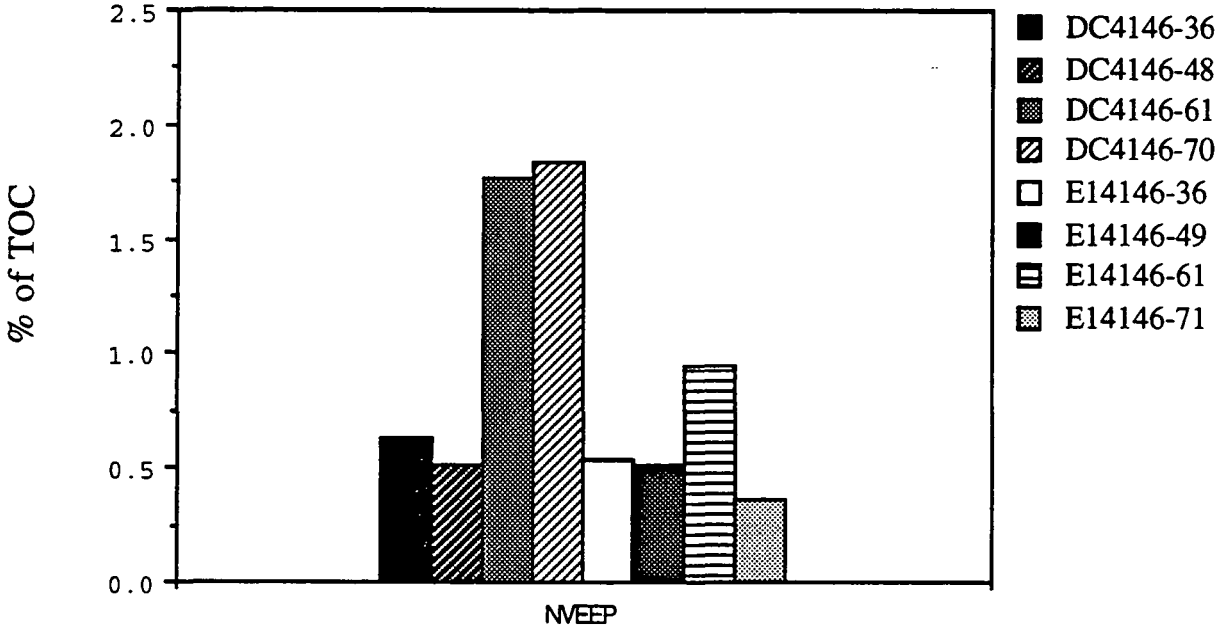


Figure 26: Percent of TOC in NVEEP.

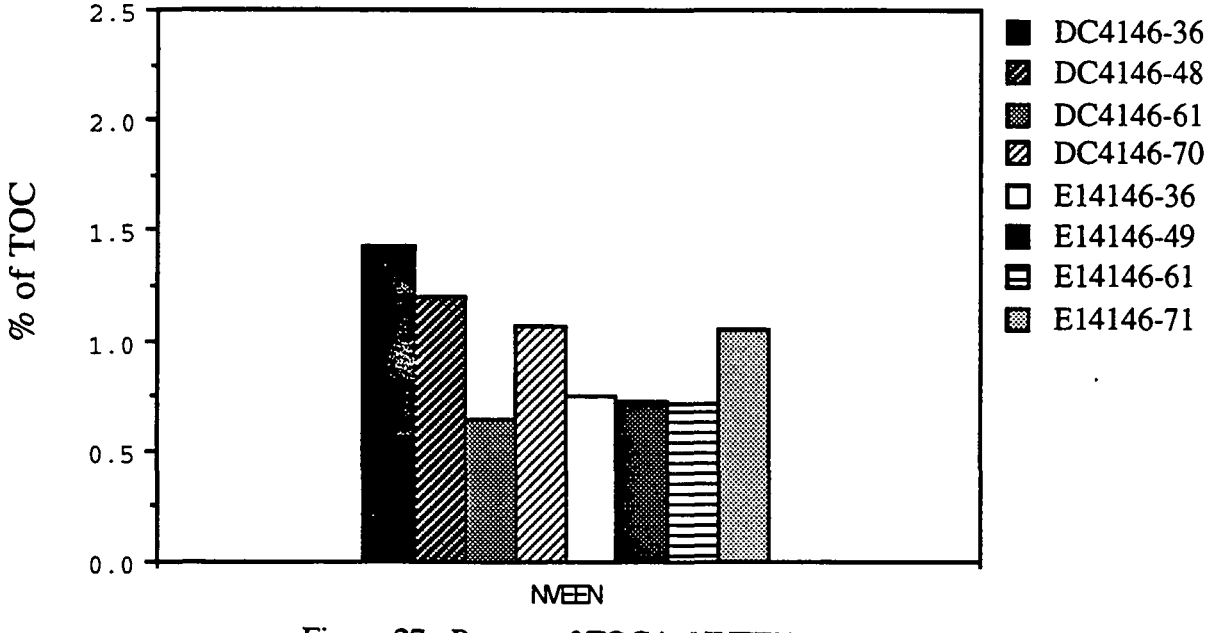


Figure 27: Percent of TOC in NVEEN.

EVALUATION OF COMMERCIALLY AVAILABLE CONDUCTIVITY SENSORS FOR BLACK LIQUOR MEASUREMENTS

PROJECT 3741

Charles E. Courchene
Blair R. Carter

ANNUAL RESEARCH REVIEW
APRIL 28, 1993

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
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ATLANTA, GA 30318

TECHNICAL PROGRAM REVIEW REPORT

PROJECT TITLE:	EVALUATION OF COMMERCIALLY AVAILABLE CONDUCTIVITY SENSORS FOR BLACK LIQUOR MEASUREMENTS
PROJECT STAFF:	Charles Courchene, Blair Carter
FY 92-93 BUDGET:	$39,000
REPORTING PERIOD:	Feb. '92-Feb. '93
DIVISION:	Chemical and Biological Sciences
FUNDING SOURCE:	AMERICAN PAPER INSTITUTE - MEASUREMENT TECHNOLOGY COMMITTEE (API-MTC)
PROJECT NUMBER:	3741

OBJECTIVE:

To evaluate commercially available conductivity sensors for their ability to accurately and reproducibly monitor alkali concentration in mill black liquors.

FY 92-93 Goals:

1. Establish a relationship between conductivity for three sensor-transmitter types and residual alkali of black liquor.

2. Evaluate the effect of velocity and temperature on conductivity for black liquor samples.

3. Conduct tests with eight black liquor samples representing batch and continuous digesters, hardwood and softwoods, and bleached and unbleached grades.

4. Write report of results.

5. Finalize details of proposal for green liquor testing.

SUMMARY

The evaluation of the conductivity sensors for black liquor was completed and will be reported as API-MTC Report No. 74 and IPST Project 3741.

Three types of conductivity sensors and supplied transmitters were evaluated for their ability to measure the alkali concentration of mill black liquors.

The three sensor types were:

- Four electrode
- Flow-through electrodeless
- Insertion electrodeless

The sensors and transmitters were supplied by three different suppliers and were installed and used according to the suppliers recommendations.

There was no effect on the conductivity readings from variations in flow velocity up to 9.3 feet per second in the 1" line.

The temperature of the liquor was varied from 100°C up to 160°C as it circulated in the flow loop. The temperature was stabilized at four points (105, 125, 145, and 160°C) and conductivity readings recorded. There were problems with the temperature compensation functions for each of the three instruments over this range.

The four electrode sensor (referred to as COND1) has a built-in compensation to a reference temperature of 25°C. Even with this compensation, the conductivity readings increased with increasing temperature.

The flow-through electrodeless sensor (referred to as COND2) is supplied with a compensation function to a reference temperature of 25°C. The conductivity readings were constant with increasing temperature up to about 145°C, then, the readings would decrease slightly as the temperature was raised further to 160°C.

The electrodeless sensor (referred to as COND3) is supplied with a temperature compensation for black liquor at a reference temperature of 160°C. This compensation did not work correctly as the conductivity readings consistently decreased with increasing temperature.

The black liquors were analyzed for dissolved solids, residual alkali, lignin content, sodium carbonate, sodium chloride, and sodium sulfate. Regression analysis was done to determine which of these parameters had a significant effect on the conductivity. The conductivity showed a strong linear correlation with residual alkali for all three instruments in the range 7.9-49 g/l as Na_2O. The other liquor components did not have a significant effect on the conductivity at the concentrations used in this study.

There were no differences among the three instruments in their response to alkali changes at a given temperature. The correlation coefficients of conductivity versus alkali were identical for all three.

Long-term testing consisting of two 30 day periods with continuous circulation of black liquor at 160°C was done. Shortly after the start of the first period, COND1 began to foul over as evidenced by erratic conductivity readings. The sensor was taken out and cleaned with dilute acid and reinstalled. No further problems with this sensor were encountered during the rest of the testing. Consistent readings were obtained from the other two sensors throughout this test.

INTRODUCTION

API-MTC STUDY

A study was proposed by the Measurement Technology Committee (MTC) of the American Paper Institute (API) to evaluate some of the conductivity sensors presently available.

The objective of this study was:

> To evaluate commercially available conductivity sensors for their ability to accurately and reproducibly monitor alkali concentration in process streams.

The work proposed by the Institute would evaluate several different sensor designs under the same conditions. The sensor designs to be evaluated were:

1. Four-electrode type
2. Flow-through electrodeless
3. Insertion electrodeless

The older two-electrode style was not chosen for the study.

The four-electrode design utilizes a pair of potential sensing electrodes and a pair of current electrodes. The circuitry consists of an amplitude-controlled oscillator controlled by a high input impedance amplifier-controller. The oscillator varies the amplitude output to maintain a constant excitation field in the solution as sensed by the potential sensing electrodes. The excitation field is created by the current electrodes. The current required to create the excitation field passes through a load resistor and is sensed as a voltage drop by the conductivity sensing circuit. The amount of excitation current required to maintain a constant excitation field in the solution is directly proportional to solution conductivity. If the electrodes become fouled, the AC potential at the electrodes will increase to drive the excitation field through any deposits to maintain the constant excitation field. The increase in potential compensates for the increase in interface resistance at the current electrodes.[1]

The electrodeless sensors use two toroidally wound coils encapsulated in a resistant plastic material. The process solution couples the two coils. An AC signal is applied to one toroid which induces a current in the second toroid directly proportional to the solution conductivity. The current from the second toroid is then converted to a conductivity measurement.[2]

Each of the three sensors was acquired from a different supplier. A transmitter was also supplied with each sensor. Differences in the transmitters as to their functions and adaptability to the process really made this work a study of sensor-transmitter combinations.

The Phase I testing was designed to evaluate the effects of flow, temperature, and chemical concentration. Specifically, the concentration and temperature range of kraft mill white liquors was used. The response of the sensors was measured with changes in the above variables. The major purpose of this phase was to see if there were any differences in the response of the different sensor types to the test conditions. The results of this study were reported in API-MTC Report No. 71 and summarized in the Annual Research Review report of March 25, 1992 .

The testing in Phase I showed that there was no difference in the response of the sensor-transmitters to changes in the chemical concentrations. There was also no effect from flow variations up to a velocity in the test loop of 11 feet/second. There were differences in the performance of the temperature compensation functions among the three transmitters. Multiple regression analysis showed the conductivity to be correlated with the NaOH, Na_2S, and Na_2CO_3 concentrations.

Phase II testing, which is the subject of this report, was proposed to determine the response of the sensor-transmitters to mill black liquor alkali concentrations. The long-term response of the sensors was also to be tested.

The individual suppliers of the instruments are not identified in this report, per a decision of MTC, since the work was not intended as an evaluation of suppliers but, rather, sensor-transmitter types.

EXPERIMENTAL

TEST STAND

The test stand was constructed around the Institute's 1.8 cu. ft. batch digester with a chemical circulating pump as shown in the schematic in Figure 1.

Liquor from the bottom of the digester goes into the suction of the pump. Liquor from the pump outlet goes through an indirect steam heat exchanger and is returned to the top of the digester.

The test loop was extended from a "t" in the line from the pump outlet. All piping was 1" diameter 316 stainless steel. Ball valves in the test loop and heat exchanger loop were used to control the flow split.

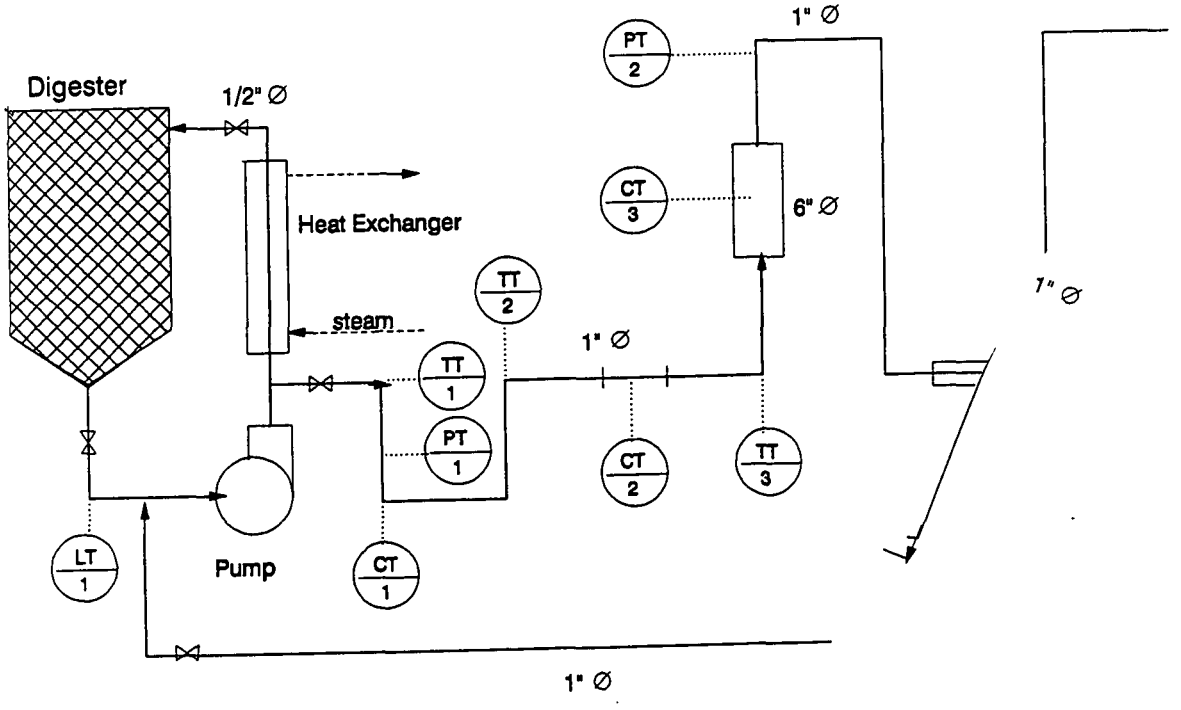

Figure 1 Test Stand

SENSOR-TRANSMITTERS

The sensor-transmitter referred to in this report as COND1 is a four-electrode style with an integral thermistor and electronics for temperature compensation to a 25°C. The sensor was installed according to the manufacturer's recommendation in a pipe line "t" with the direction of flow into the face of the sensor. COND1 is indicated in Figure 1 as CT1. The transmitter is a two-wire model with digital display and 4-20 mA output proportional to the conductivity.

The sensor referred to as COND2 is a flow-through electrodeless type mounted on the outside of a 1" diameter Teflon-lined, carbon steel pipe. COND2 is shown in Figure 1 as CT2. A separate RTD is furnished for measuring the process temperature for compensation to a standard of 25°C. The transmitter is a microprocessor-based unit with factory preset values for cell constant, range, and temperature coefficient. The cell constant and temperature coefficient were determined with NaOH solutions as reported in API-MTC Report No. 71. They were not changed for this study.

COND3 (CT3) is an insertion type electrodeless sensor. The operating principle is the same as the COND2 sensor. COND3 has the toroids mounted on the end of a stem. The total length is about 6". Since this cannot be accommodated in a 1" pipe, a pipe expansion was built and installed in the test loop. The pipe expansion was 6" in diameter with a flanged face. The transmitter for is a microprocessor-based unit and comes supplied with several measurement and compensation curves in the microprocessor. These are selectable by a code on the keypad. Three curves are standard and supplied with the transmitter. These are 0-15% NaOH at 25°C, 0-20% NaOH at 100°C, and black liquor at 160°C. The module used for the testing was black liquor at 160°C. The unit comes calibrated from the factory, and no extra calibration was done on installation. An external RTD was used for temperature measurement and compensation.

Other instrumentation included a mag flow meter, pressure transducers, RTD temperature sensors, and a level transmitter. A circulating pump with a variable speed drive was used for all testing.

Data acquisition was done with a 386-20mHz computer and a process control software package.

RESULTS

LIQUOR ANALYSIS

Each of the mill liquors was tested for the components as described in Part II. The sources of the liquors are shown in Table I and the analysis results in Table II.

TEMPERATURE COMPENSATION

Since conductivity varies directly with temperature, it is important that conductivity readings be compensated to a standard temperature, particularly in a process where the temperature may fluctuate. The nominal standard used in many references is 25°C. Both COND1 and COND2 use this reference temperature. The COND3 transmitter has several switch-selectable options for temperature compensation. The supplier maintains that it is more accurate to use a temperature compensation close to the actual process temperature rather than extrapolating back to 25°C. With a higher reference temperature for compensation, the conductivity span is also greater for a given alkali range, and consequently, the resolution may be greater.

The temperature compensation functions with each of the three sensor-transmitters were found to differ in accuracy.

The COND1 sensor-transmitter is supplied with electronics for temperature compensation to 25°C. The conductivity response versus temperature from 100°C to 165°C is shown in Figures 2 and 3 for each of the eight mill liquors. As can be seen, the conductivity increased steadily with increasing temperature. The temperature variation was somewhat less from 145°C up to 165°C. Similar variations in conductivity with temperature were also seen with the white liquor testing in Phase I for COND1.

It should be noted that the temperature sensor for COND1 is a built-in thermistor in the tip, while both COND2 and COND3 used external RTDs for a faster response. In an installation where temperature may vary, a COND1 type sensor could use an external RTD for greater sensitivity, or an uncompensated signal could be used with correction by a compensation algorithm determined by testing in the particular process.

TABLE I
Mill Black Liquor Source

Sample No.	Source
1	Bleachable Grade Southern SW - Batch Digester - First Stage Filtrate
2	Bleachable Grade Western SW - Kamyr MCC Digester - Bottom Circulation Loop
3	Bleachable Grade Western SW - Kamyr MCC Digester - MCC Loop
4	Bleachable Grade Western SW - Kamyr MCC Digester - Impregnation Vessel Loop
5	Bleachable Grade Western SW - Kamyr MCC Digester - Liquor to Recovery
6	Sack Kraft Southern SW - Kamyr Digester - Upper Cook Zone
7	Bleachable Grade Southern SW - Kamyr Digester - Upper Cook Zone
8	Bleachable Grade Southern HW - Kamyr Digester - Upper Cook Zone

TABLE II
MILL BLACK LIQUOR ANALYSIS

Sample No.	%DS	%SS	RA	L_{280}	Na_2CO_3	Na_2SO_4	NaCl	Na	Ash	Viscosity	Sp. Gravity
1	12.2	0.003	7.75	111	4.74	2.53	0.95	27.1	36.4	1.51	1.065
2	16.6	0.015	18.2	28	9.77	5.59	1.28	30.5	43.3	1.92	1.105
3	15.1	0.002	17.1	29	7.90	4.13	0.83	27.1	37.4	1.98	1.090
4	14.6	0.026	19.2	28	10.18	4.27	1.01	31.1	76.8	1.74	1.095
5	18.5	0.028	11.1	86	10.00	4.94	0.99	25.2	53.4	2.40	1.105
6	17.4	0.002	17.6	29	6.49	4.15	0.52	32.2	47.2	2.14	1.105
7	16.0	0.059	27.0	29	12.60	3.00	1.70	27.0	80.8	2.13	1.110
8	16.1	0.031	23.5	32	5.85	1.12	0.99	35.5	38.8	3.52	1.110

%DS = % dissolved solids
%SS = % suspended solids
RA = g/l residual alkali as Na_2O
L_{280} = g/l lignin

Na_2CO_3 = %/DS as Na_2O
Na_2SO_4 = %/DS as Na_2O
NaCl = %/DS as Na_2O
Na = %/DS total sodium as Na_2O

Ash = %/DS
Viscosity = cps at 25°C

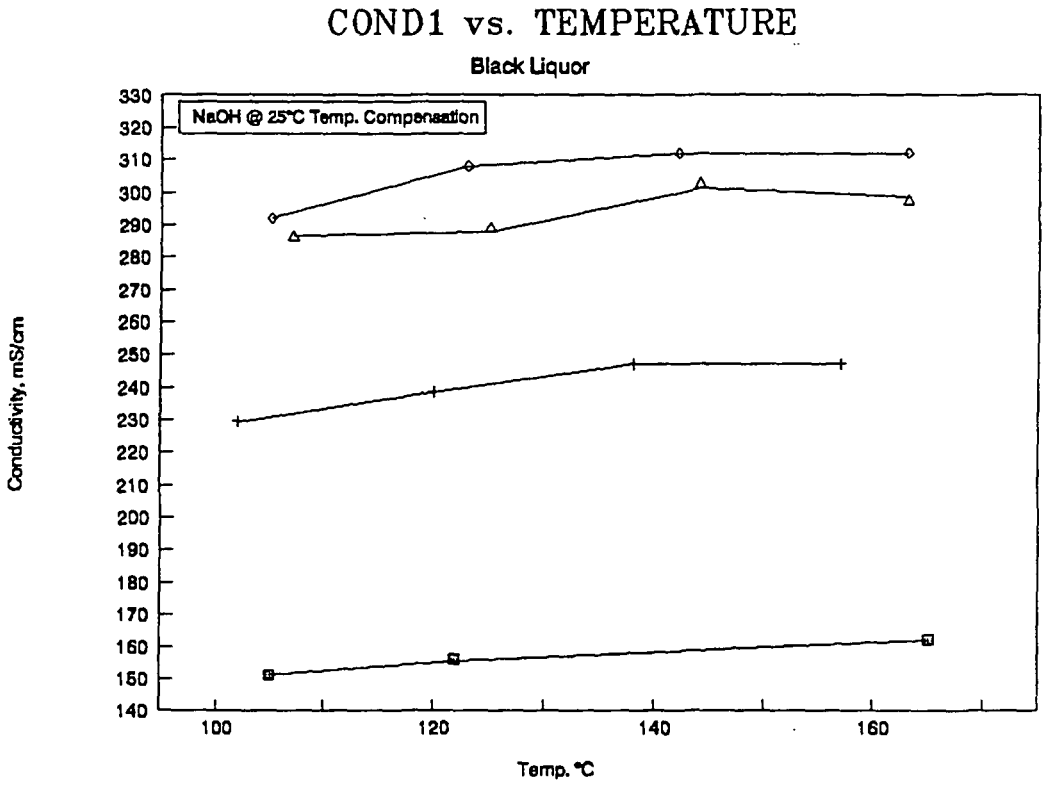

Figure 2

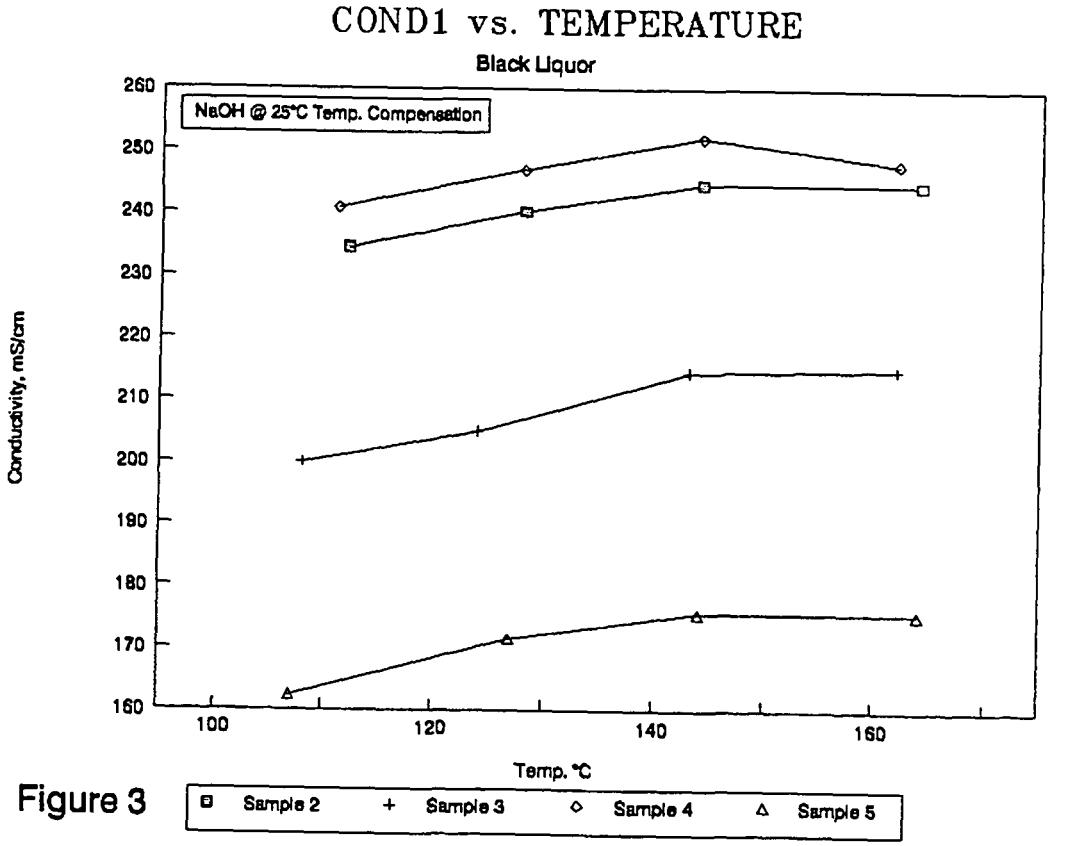

Figure 3

The COND2 sensor-transmitter comes with a factory preset temperature compensation coefficient of 2%/°C for a reference temperature of 25°C. The supplier recommends, when possible, to do preliminary testing with the instrument and determine a compensation coefficient for the particular process. At the beginning of the Phase I testing, the conductivity response was recorded at different temperatures with no temperature compensation for strong NaOH solutions. The temperature coefficient was calculated to be 2.11%/°C. This value was entered into the transmitter and used for all subsequent testing.

The response of COND2 versus temperature is shown in Figures 4 and 5. The conductivity showed little or no variation up to about 145°C with a small negative variation for most samples from 145°C up to 165°C.

COND3 had a built-in temperature compensation for black liquor at a reference temperature of 160°C. The response of COND3 with temperature is shown in Figures 6 and 7. This instrument had a consistent negative variation in the conductivity with increasing temperature.

The supplier has responded to this by supplying similar units with a kit to correct the compensation. They also have a newer model transmitter which is supposed to have a more reliable temperature compensation. No changes were made to the unit used for this testing during the course of the study.

Cool Down Test

A test was done with one liquor sample to see if the temperature response could be reproduced by cooling the liquor down after heating to the maximum temperature of 165°C. This was to verify that the variations in conductivity readings were a function of temperature changes and not some irreversible reactions in the liquor from heating to a high temperature. The results are shown in Figure 8. Sample 7 liquor was used. For each sensor, there are two curves showing the conductivity versus temperature. One for heat up and one showing the response as the sample cooled down. As can be seen, each sensor showed a nearly equal response of conductivity versus temperature for heating or cooling of the liquor.

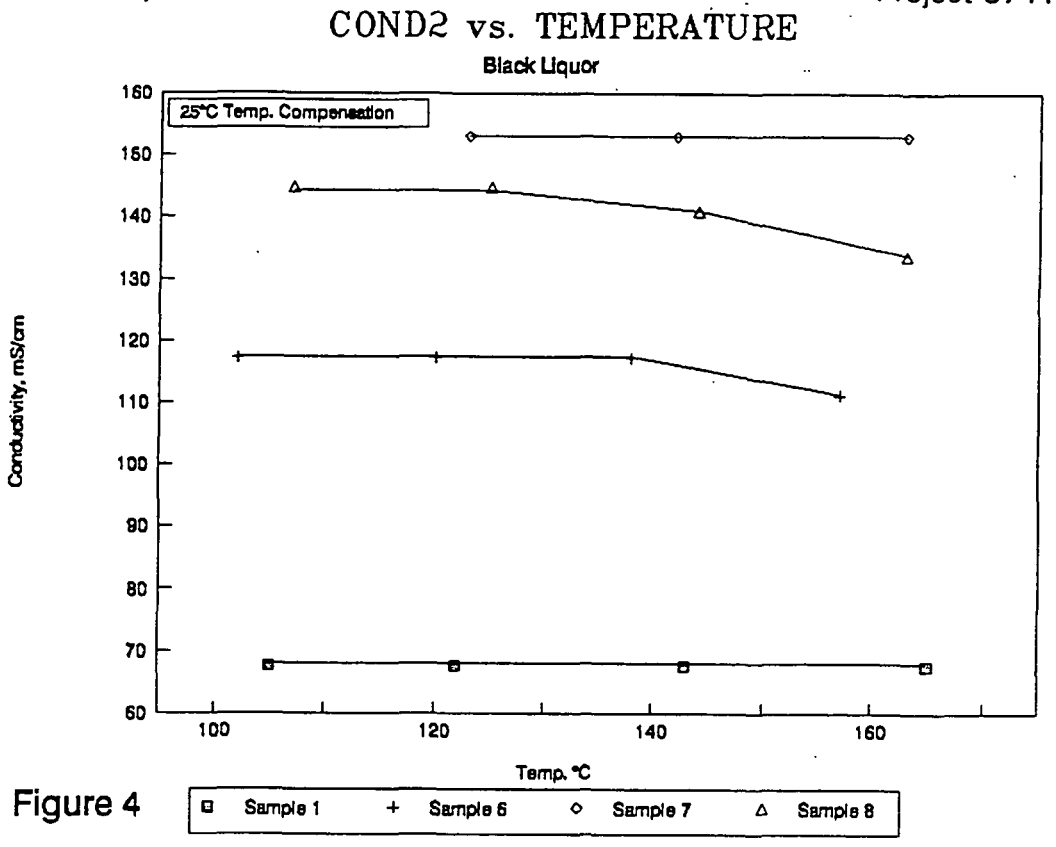

Figure 4

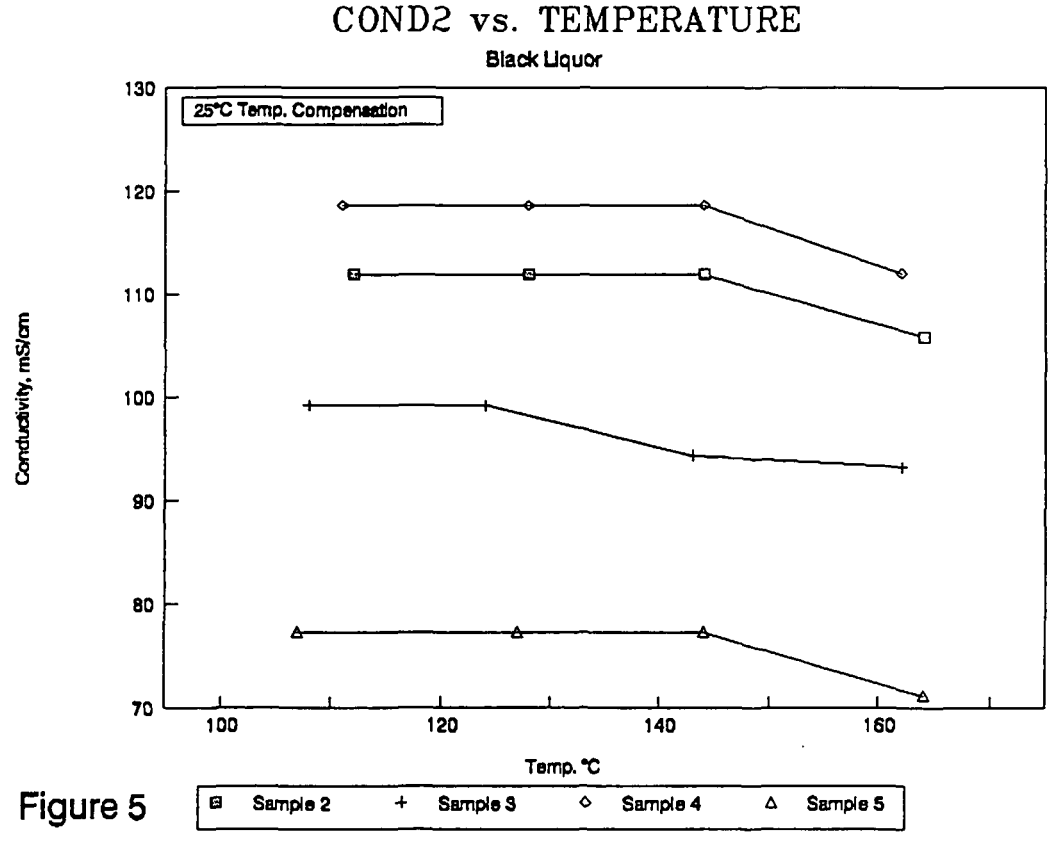

Figure 5

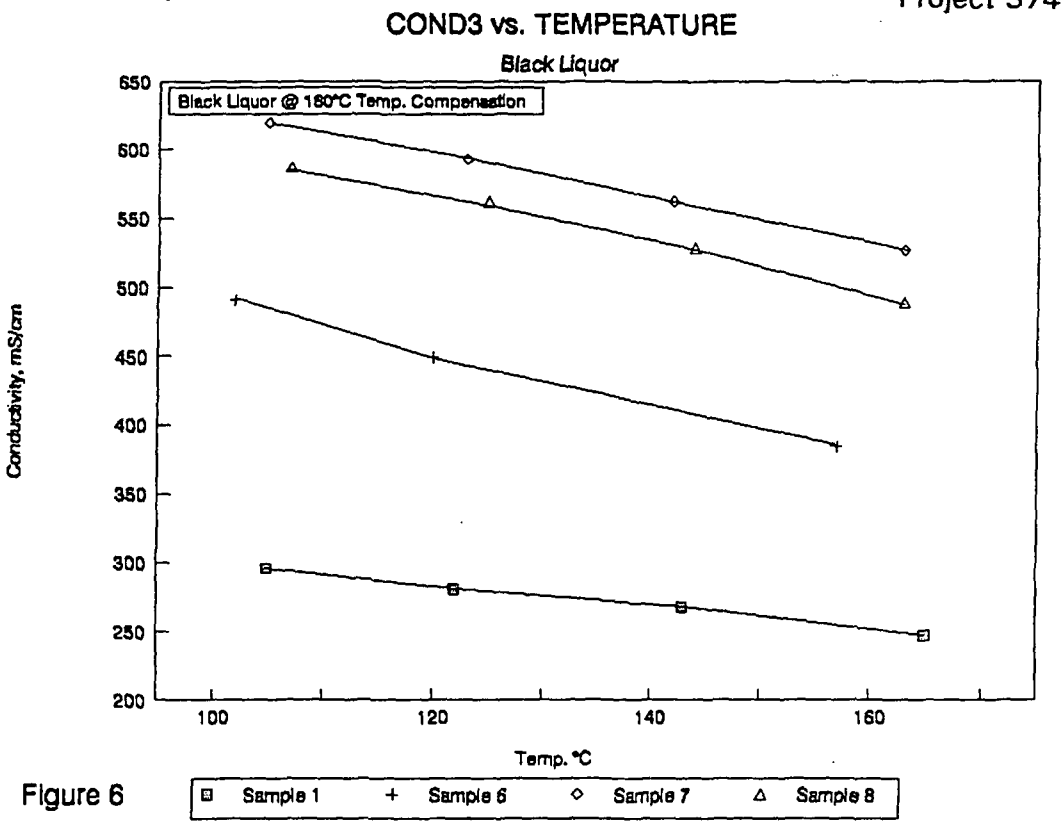

Figure 6

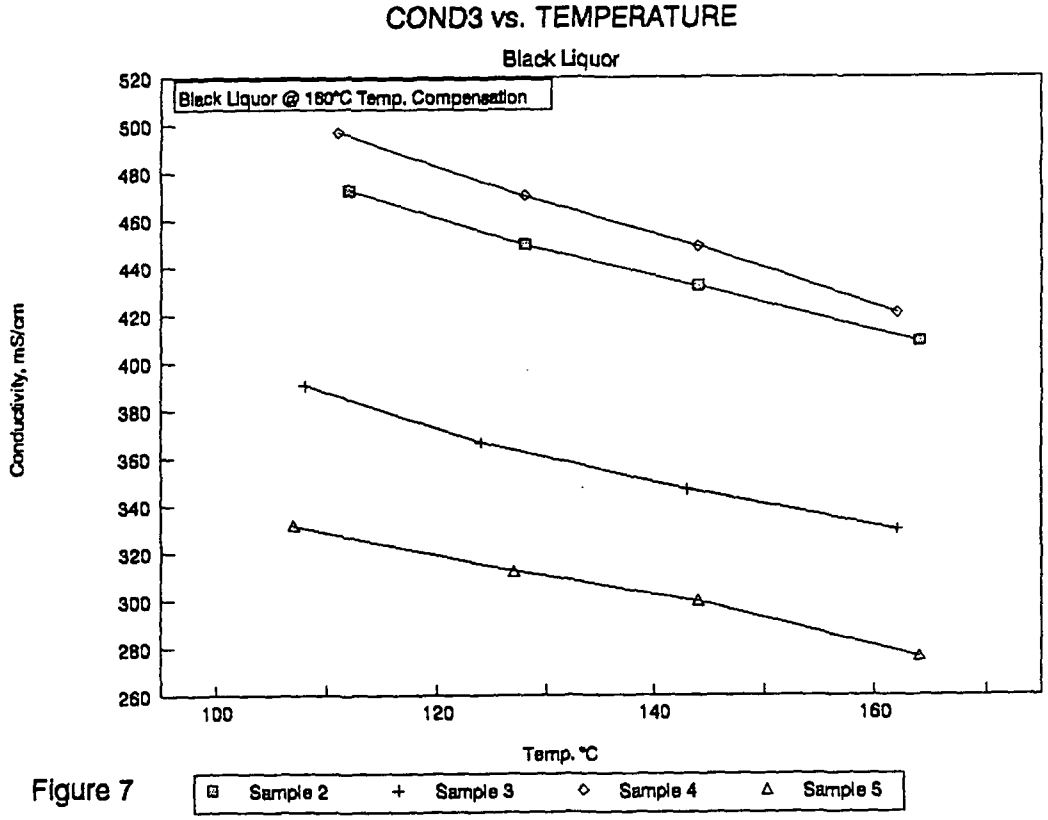

Figure 7

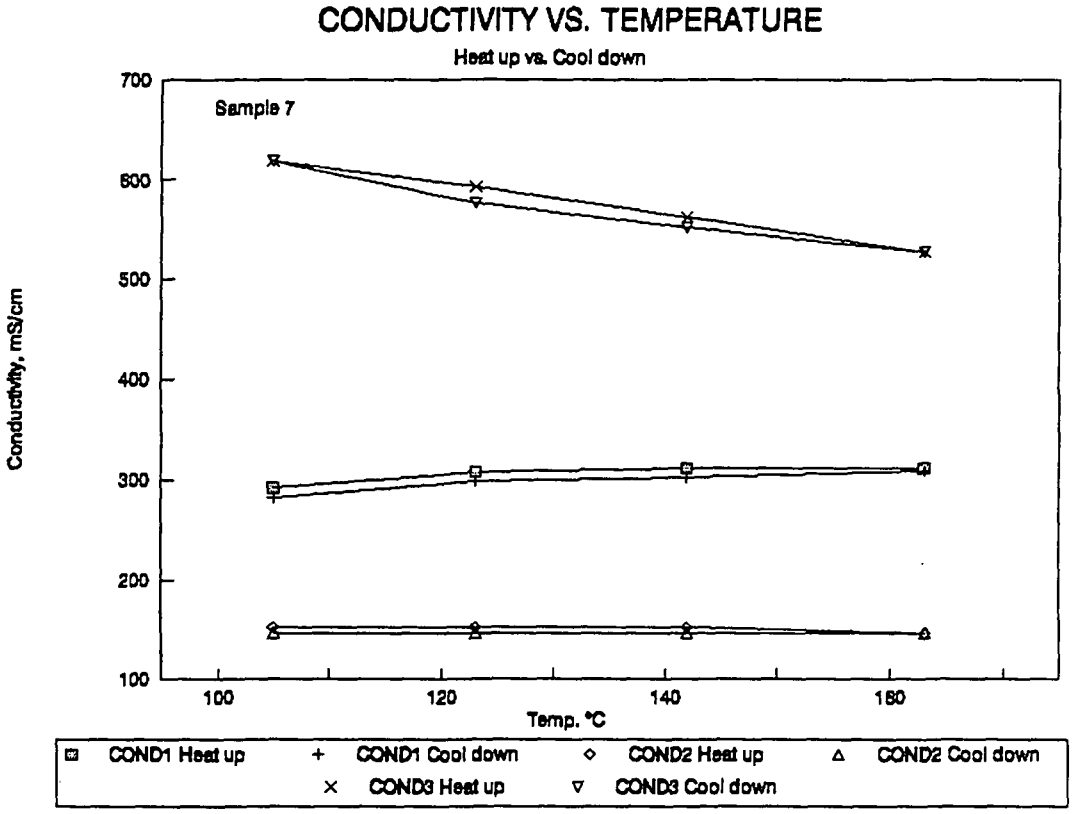

Figure 8

Direct Steam Heating

The effect of heating with direct steam was tested with Sample 8. Steam was injected directly into the bottom of the digester and the conductivity response as a function of temperature was recorded. The results are shown in Figure 9. The conductivity response for indirect heating of the same sample is also shown. The conductivity response versus temperature shows the same variations for the respective sensors-transmitters as described above. The conductivity with direct steaming is less at a given temperature than the corresponding conductivity with indirect heating. The drop in conductivity with direct heating can be found to be directly proportional to the decrease in dissolved solids concentration as a result of dilution of the liquor by steam condensation. This is shown in Table III. The ratio of the dissolved solids at each temperature to the initial concentration at 25°C is shown along with the ratio of the conductivity readings for direct and indirect heating.

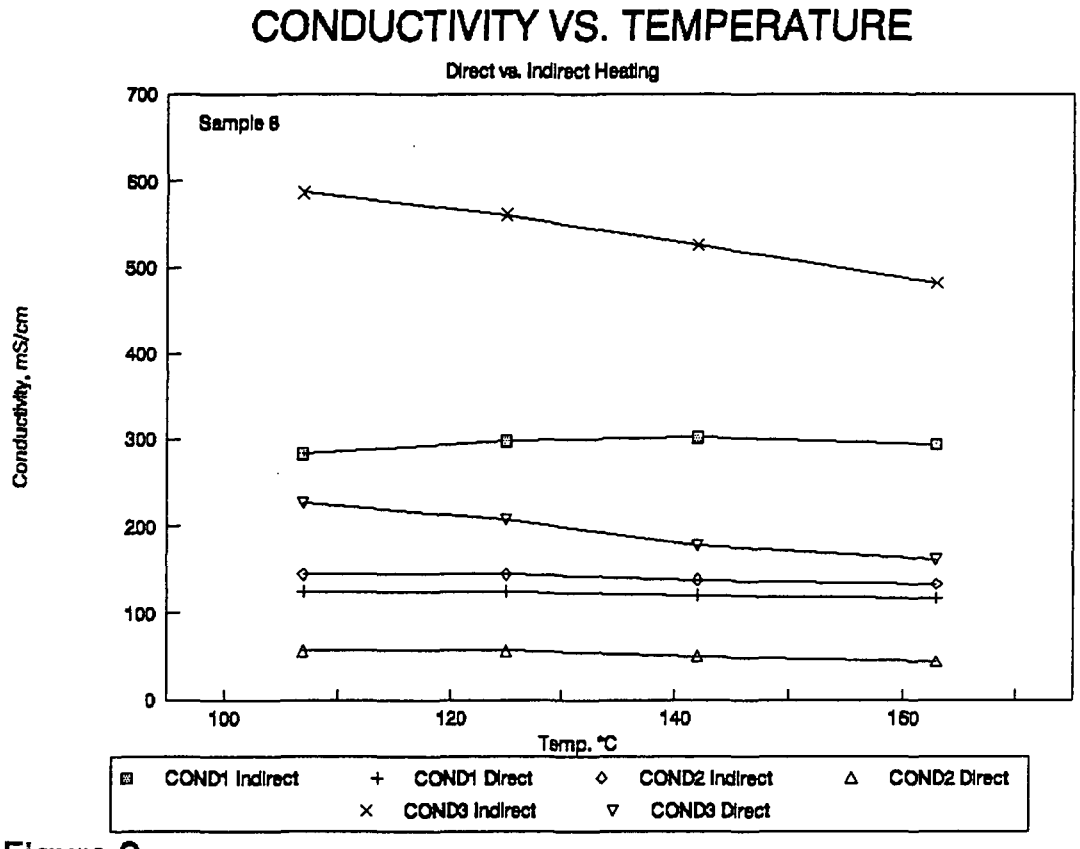

Figure 9

TABLE III
Dissolved Solids Concentrations During Direct Steaming

Temperature	%Dissolved Solids	DS Ratio COND1	Cond. Ratio (direct/indirect) COND2		COND3
25°C	15.4	1.0			
107°C	6.13	0.398	0.440	0.391	0.387
122°C	6.10	0.396	0.419	0.391	0.371
142°C	5.46	0.355	0.398	0.364	0.340
153°C	5.08	0.330	0.392	0.328	0.331

FLOW

For the first three liquors tested, the flow was varied from 9-10 gpm up to 25-27 gpm. This corresponds to a velocity range in the 1" line of 3.3 fps to 9.3 fps. As with the white liquor, there was no variation in the conductivity over the flow and velocity range tested.

ALKALI CORRELATION

Linear regression analysis was done on the data to determine if a correlation exists between residual alkali and conductivity. Additional tests were run with Samples 7 and 8 where additional caustic (NaOH) or carbonate (Na_2CO_3) was added to the liquors; then, conductivity data were collected as with the original samples. This was done to provide additional points for regression analysis and test the linear correlation between the alkali and conductivity. The concentrations of the liquors fortified for this testing are shown in Table IV.

Table IV
Chemical Concentration of Fortified Liquors

Sample No.	Residual Alkali g/l	Na_2CO_3 g/l
7	27.0	15.3
7A	32.3	15.0
7B	41.4	13.5
8	23.5	19.0
8A	36.0	18.3
8B	49.0	19.0
8C	49.0	24.0

Multiple regression analysis was done on the data to determine which of the measured liquor components have a significant effect on the conductivity. It was found that the residual alkali concentration was strongly significant, while the other sodium salts and the lignin concentration were not at the levels used in this study. It is possible that ions such as carbonate may have an effect on conductivity if present in significant quantities.

The residual alkali showed a strong linear correlation with conductivity for all three instruments with R^2 values of 0.98.
The correlation was found to be equally significant at each of the temperatures where measurements were made.

The correlations of the conductivity versus residual alkali for COND1 at temperatures of 125, 145, and 160°C are shown in Figures 10-12. Because of the imperfect temperature compensation for this sensor-transmitter, the regression equation and the conductivity range are different at each temperature. The results at 145°C are nearly similar to those at 160°C, however, because the temperature versus conductivity curve flattens out above 145°C as seen previously in Figures 2 and 3.

OW

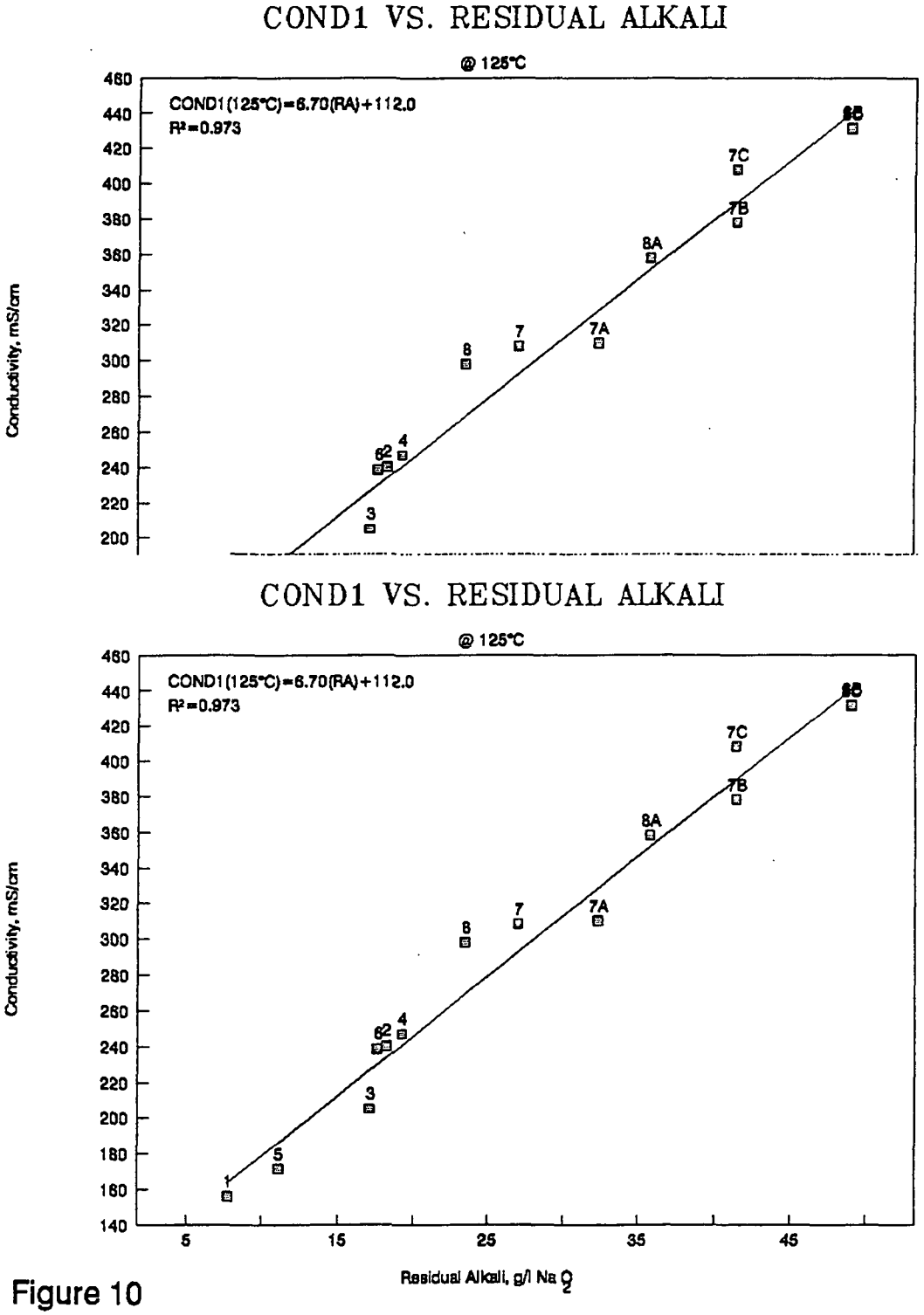

Figure 10

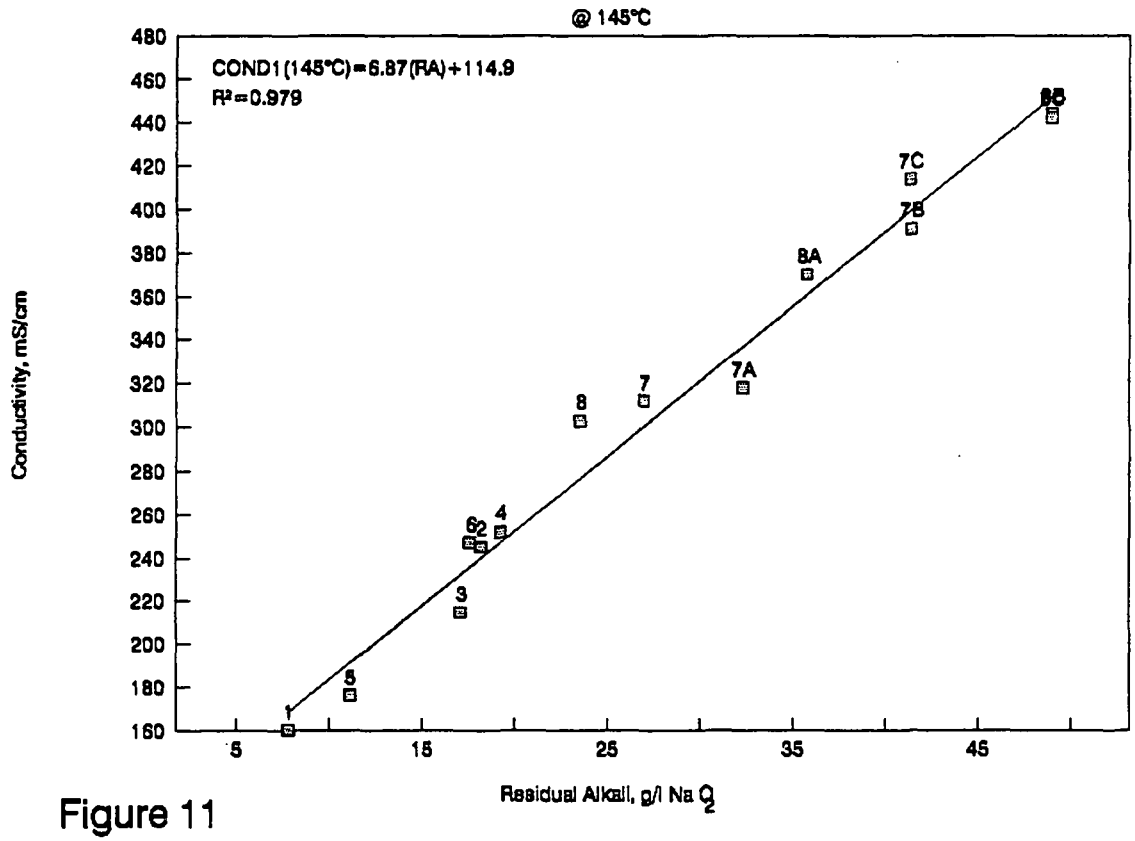
COND1 VS. RESIDUAL ALKALI
@ 145°C
COND1 (145°C) = 6.87 (RA) + 114.9
R² = 0.979
Conductivity, mS/cm
Residual Alkali, g/l Na2O
480
460
440
420
400
380
360
340
320
300
280
260
240
220
200
180
160
5
15
25
35
45
1
5
3
6
2
4
8
7
7A
8A
7B
7C
8B

Figure 11

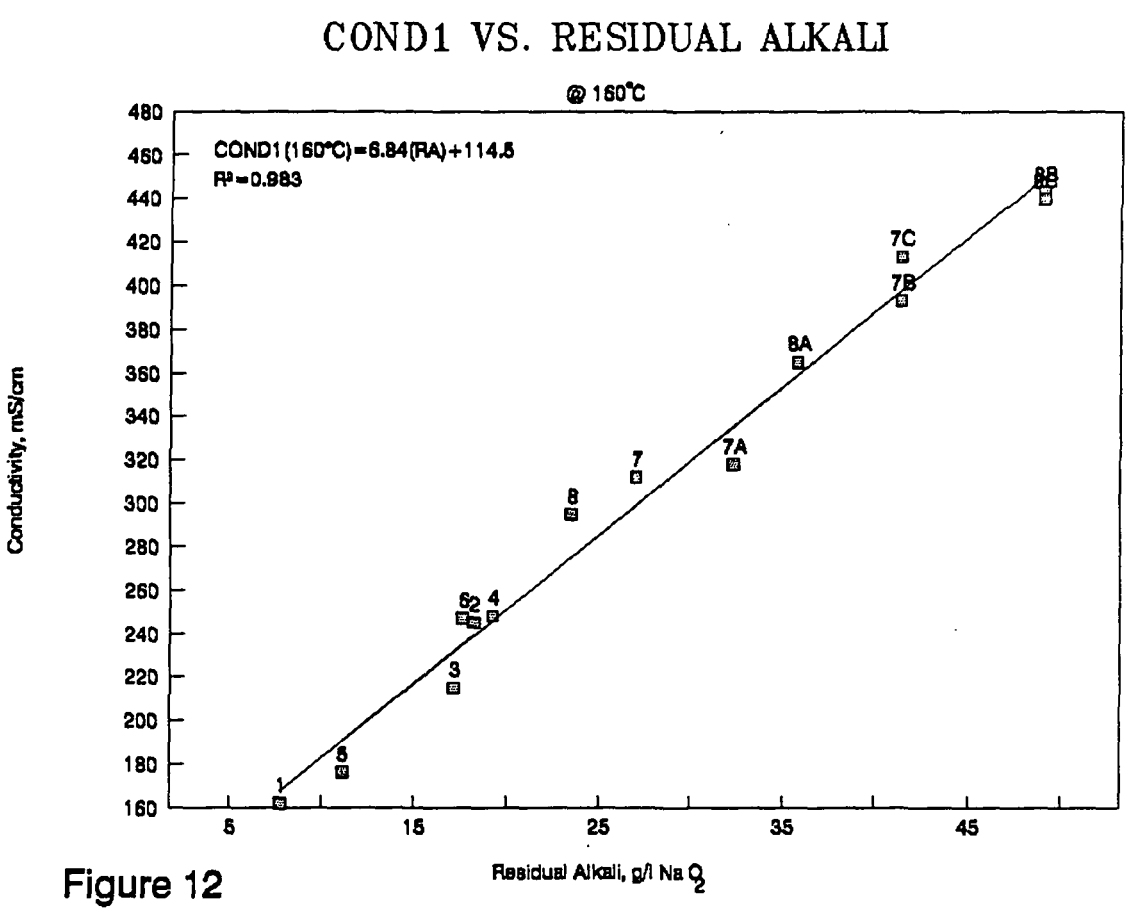

Figure 12

The results for COND2 are shown in Figures 13-15 for each temperature. There were some slight differences in the regression equations at each temperature, also because of imperfect temperature compensation. The conductivity range for COND2 spanned by the residual alkali concentration is about 150 mS/cm, while the range for COND1 is almost 300 mS/cm. While COND1 and COND2 are compensated to the same temperature of 25°C, COND1 has a greater temperature variation so that at the temperature range used here the response of COND1 has diverged considerably from that of COND2 at an equal alkali level.

The correlations for COND3 versus residual alkali at each temperature are shown in Figures 16-18. The regression equations are somewhat different at each temperature, also because of the temperature compensation variation for this instrument. The conductivity range for COND3 over the range of residual alkali tested is approximately 550 mS/cm. The wider range compared to COND1 and COND2 is the result of the higher temperature compensation of 160°C used with COND3.

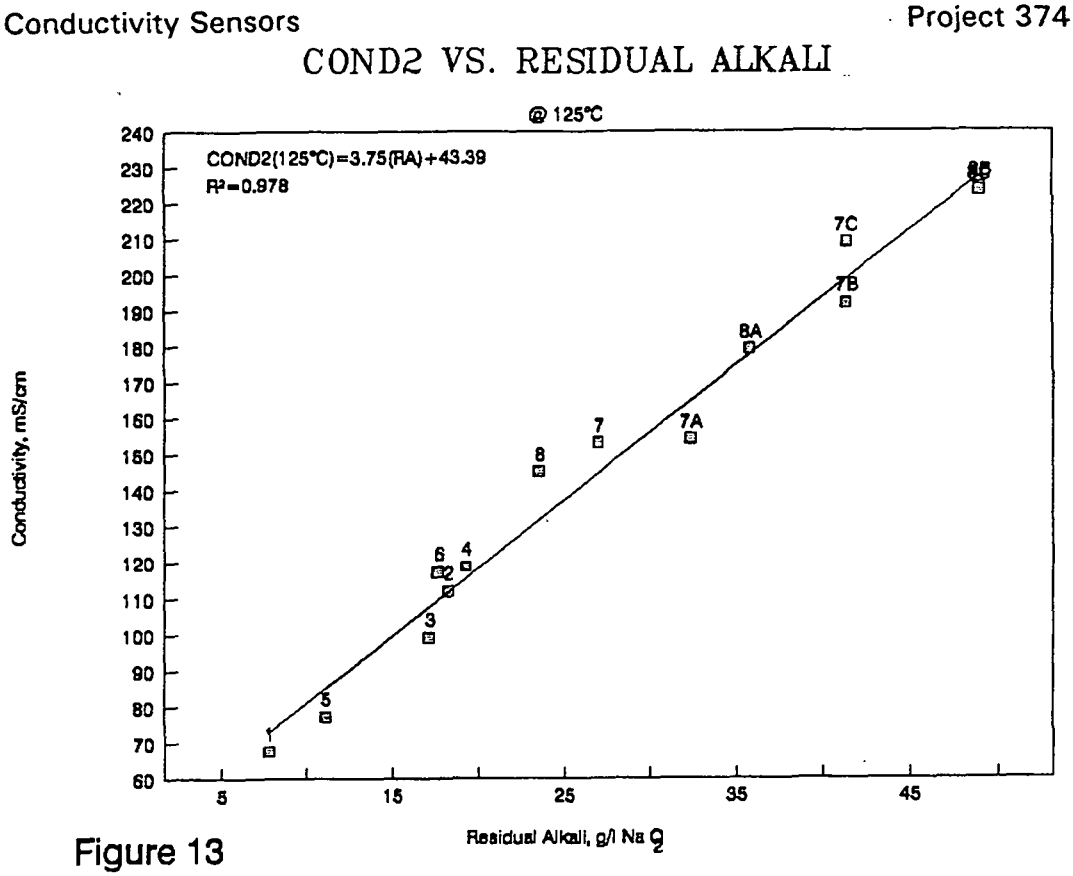

Figure 13

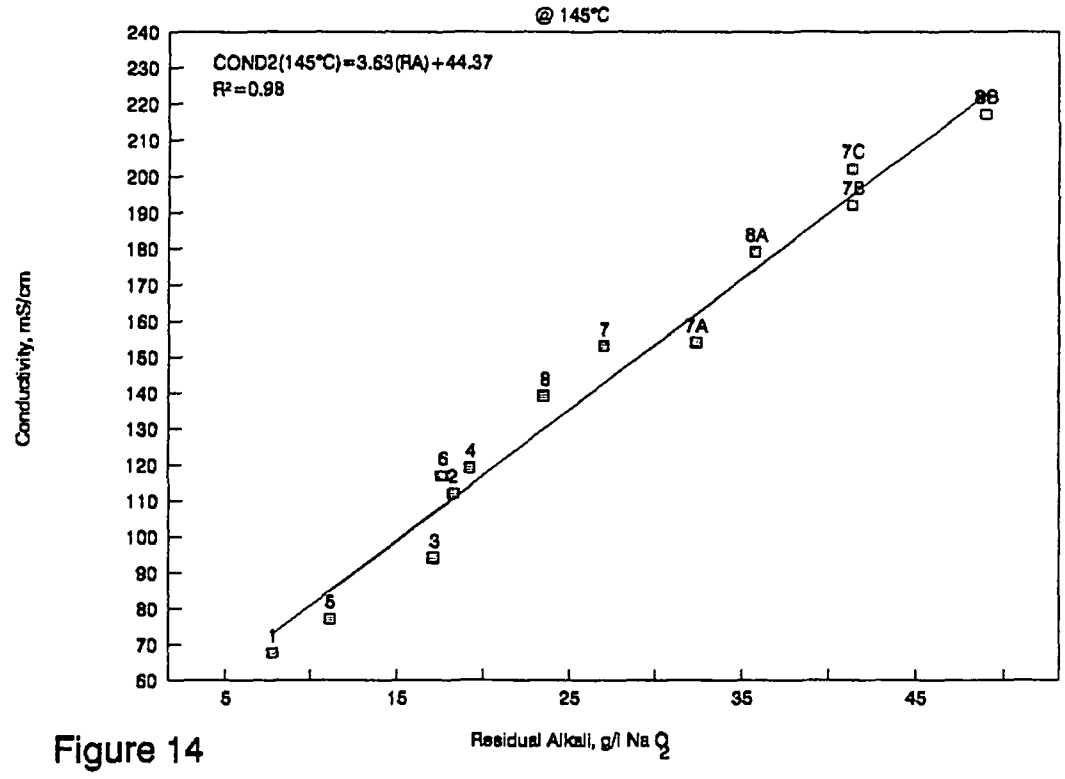

Figure 14

COND2 VS. RESIDUAL ALKALI

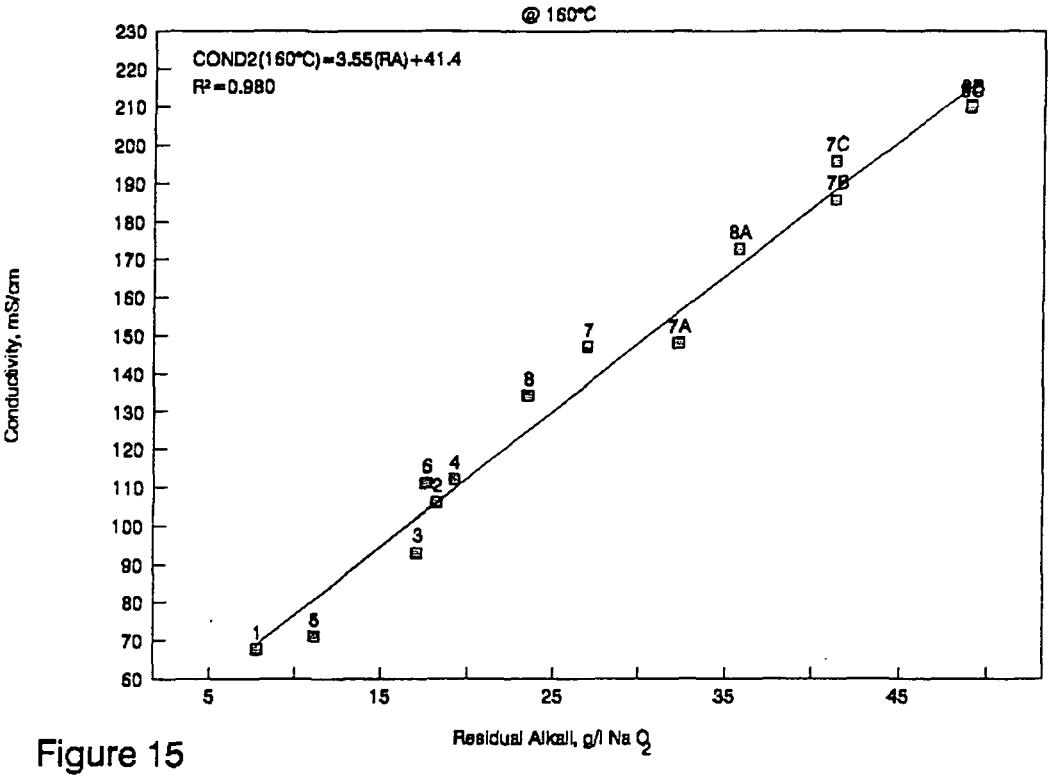

Figure 15

COND3 VS. RESIDUAL ALKALI

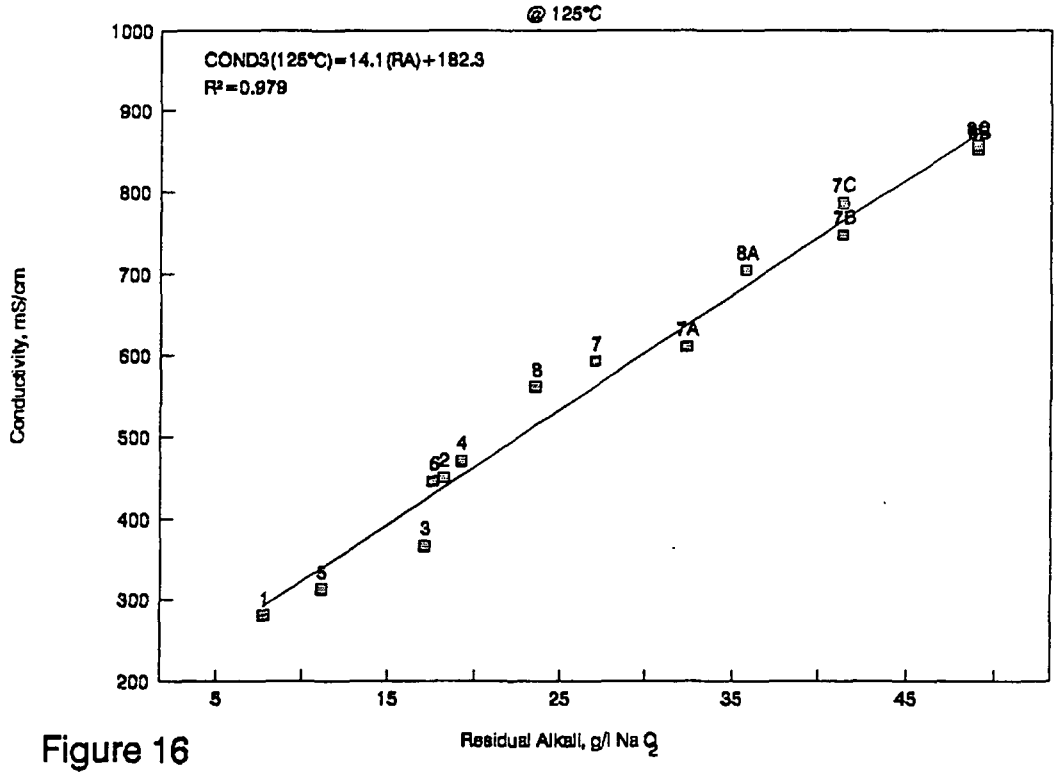

Figure 16

COND3 VS. RESIDUAL ALKALI

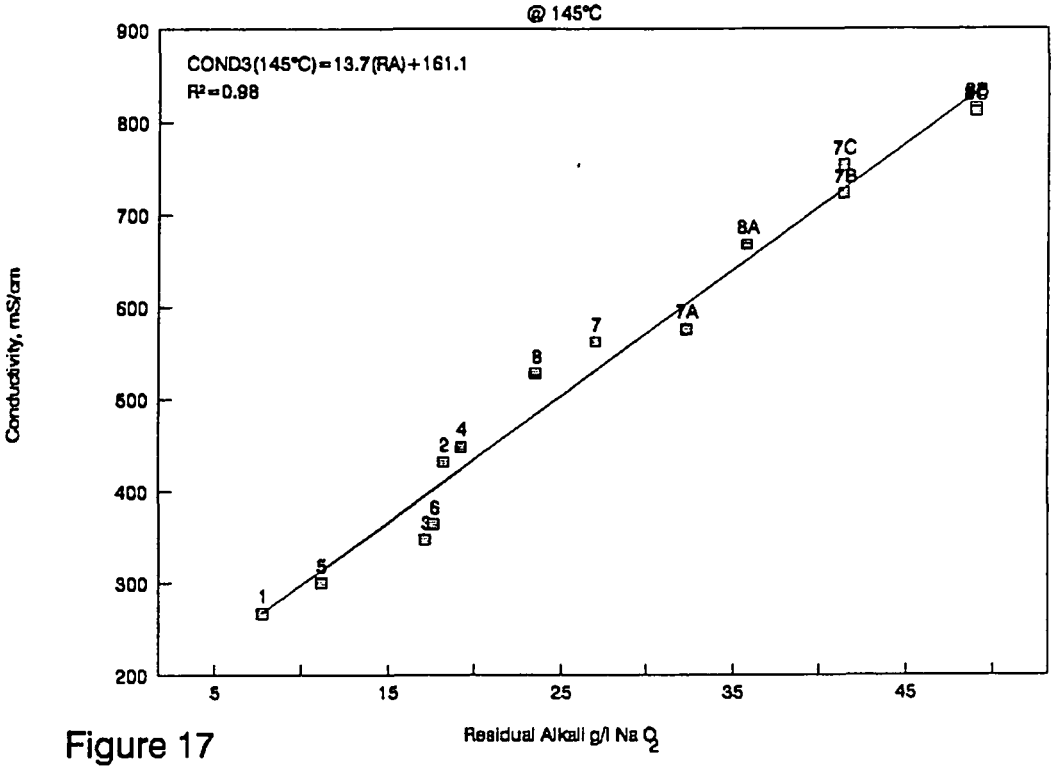

Figure 17

COND3 VS. RESIDUAL ALKALI

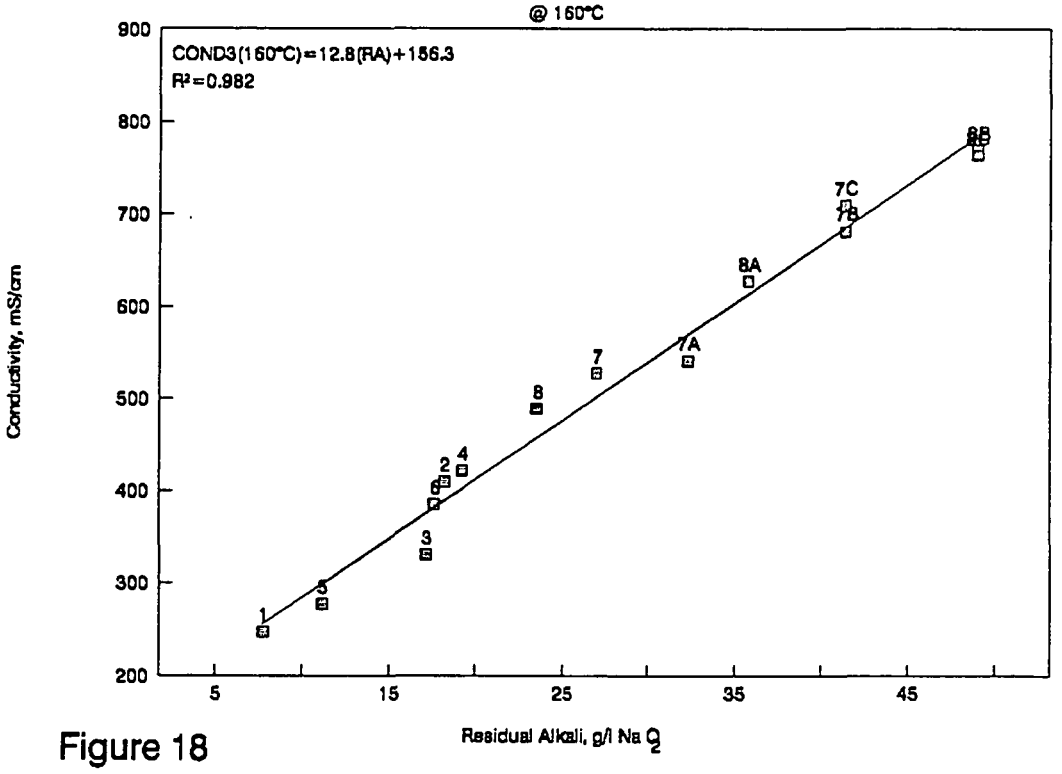

Figure 18

What is evident from comparing the responses of all three sensor-transmitters is that there is no difference in their ability to measure the residual alkali at a given temperature. The correlations for all three are nearly equal. The variations from linearity in the data points are nearly identical for all three sensors. It is possible that the variation may be attributed more to the liquor analysis than the conductivity measurements themselves.

The correlations for residual alkali expressed in terms of conductivity are shown in Table V.

TABLE V
Correlation of Residual Alkali and Conductivity

125°C

RA = 0.149(COND1)-16.72

RA = 0.267(COND2)-11.57

RA = 0.0709(COND3)-12.93

145°C

RA = 0.146(COND1)-16.72

RA = 0.0.275(COND2)-12.2

RA = 0.0730(COND3)-11.76

160°C

RA = 0.46(COND1)-16.74

RA = 0.282(COND2)-11.66

RA = 0.0781(COND3)-12.21

RA = Residual alkali as g/l Na_2O

LONG-TERM TESTING

Long-term testing was done with Sample 8 after the test runs described above were completed. The sensors were cleaned prior to the start of the black liquor testing but were not cleaned again prior to the long-term testing. This sample was allowed to circulate continuously at 20 gpm and a target temperature of 160°C. This testing was restarted several times after leaks developed in the piping and liquor was lost. The first continuous 30 day period results are shown in Figure 19.

After four days into this testing, the conductivity reading from COND1 became very erratic, oscillating as much as 100 mS/cm either high or low of the baseline reading. This occurrence was not noticed for several days since it was over a holiday weekend. At this point, it was decided to take the sensor out of the line to see if it was becoming fouled. The system was allowed to cool down and the piping valved off. The sensor was taken out of line and was seen to have a very thin coating of fine black particles. The tip was cleaned with dilute (0.1 N) HCl. It was put back into the line, and the system was heated back up. COND1 returned to its original performance, and no further problems were encountered.

The problems with temperature compensation described earlier are also evident in Figure 19. The first variation in readings in COND1 and COND3 marked as "Boiler down" occurred when the system was cooled down to take COND1 out for cleaning. The second variation marked as "Boiler down" was when the boiler was shut down for two days for maintenance and the system cooled down. The resulting variations in the conductivity readings, again, are the result of imperfect temperature compensation functions.

A second continuous run of 30 days was also done, shortly after the first run. This is shown in Figure 20. There were no obvious problems during the test. The readings were steady with only some slight variations due to temperature fluctuations.

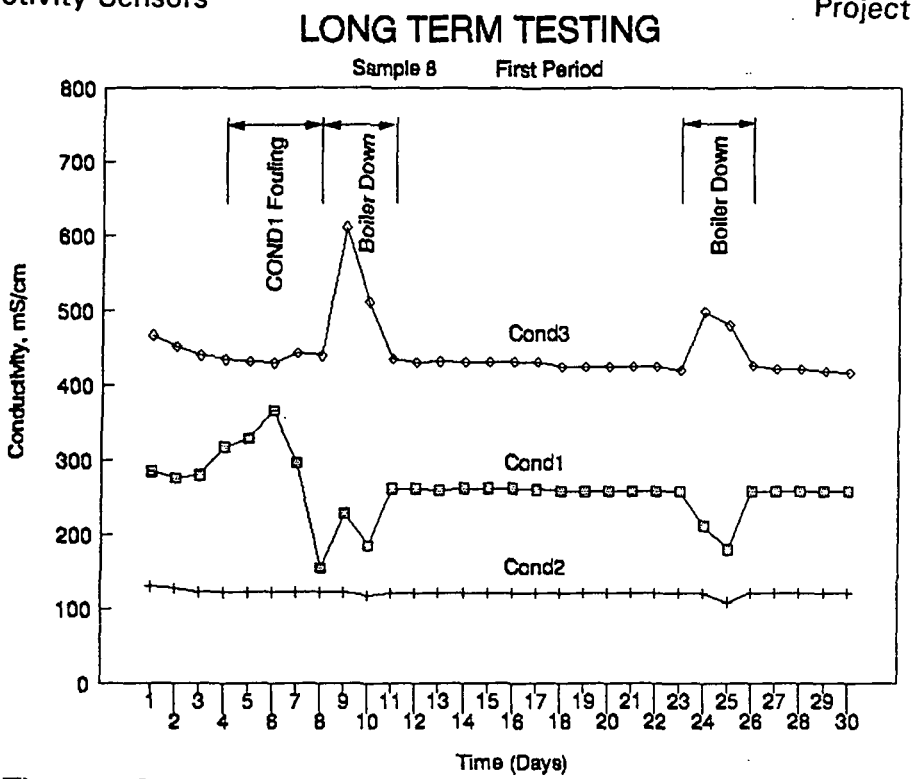

Figure 19

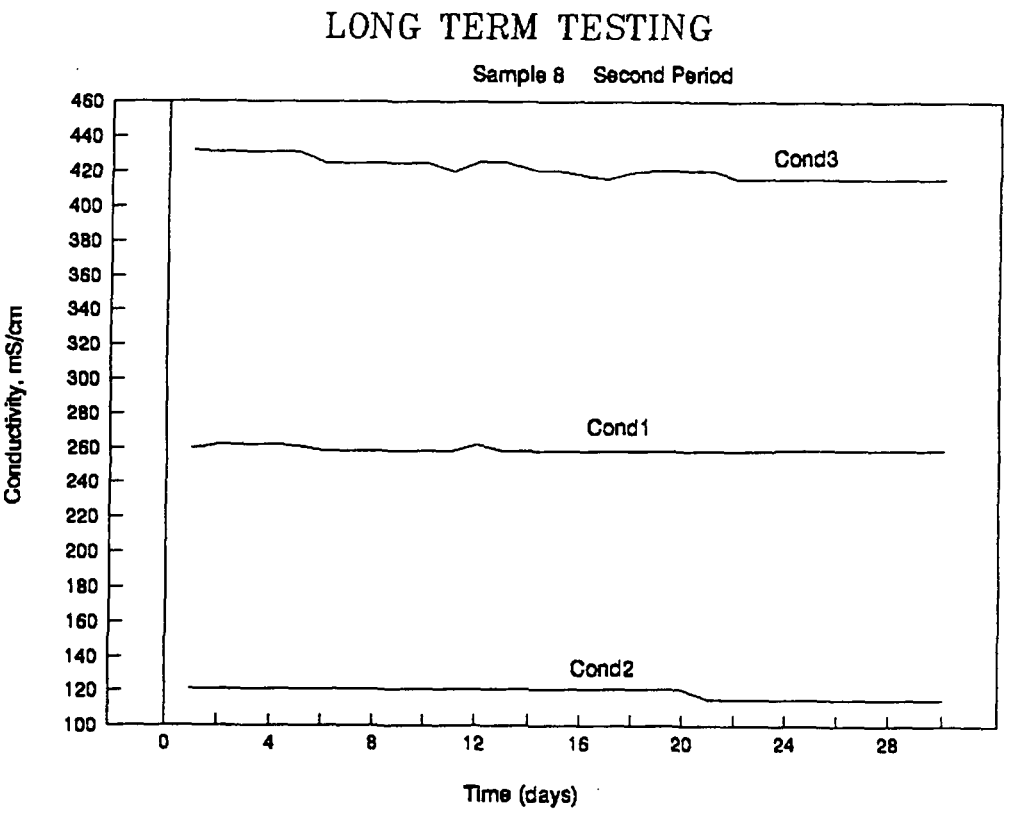

Figure 20

CONCLUSIONS

The conductivity sensors and transmitters tested here showed a strong linear correlation between conductivity and residual alkali. There were no differences in the ability of each of the instruments to measure the alkali concentration. All three responded equally to changes in the alkali concentration.

The temperature compensation functions did not perform properly over the range of 100°C to 160°C for all three sensors. COND1 readings increased consistently with increasing temperature. COND2 readings were constant up to about 145°C then decreased slightly up to 160°C. COND3 readings decreased consistently with increasing temperatures.

For mill applications where varying temperatures may be encountered, the temperature compensation function must be carefully considered. An external RTD for temperature measurement would be preferable to an internal thermistor sometimes supplied with the sensors. Testing in a specific application could be done with a given instrument to derive a temperature compensation algorithm that could be used in a DCS control system to correct an uncompensated signal from the sensor. With proper temperature compensation, any of these instruments should be able to give reliable determinations of residual alkali.

Fouling is always a potential problem with conductivity sensors. Long-term testing showed that the four electrode sensor is more prone to fouling. A simple acid cleaning restored the sensor to its original performance.

FUTURE WORK

Continuing work has been planned for studying the response of the instruments in green liquor applications. This is felt to be a valuable application for conductivity measurements since the makeup of the white liquor can be directly affected at this stage. There are more potential interferences, however, from carbonate and other ion sources.

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LIPOPHILICITY OF A SYNTHETIC BLEACHED KRAFT EFFLUENT

Student Research

Environ. Sci. Technol., in press

Robert Diercks
Sujit Banerjee

ANNUAL RESEARCH REVIEW
APRIL 28, 1993

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
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This section is intended to inform Institute membership about a student research project which concerns bleaching chemistry and should have general interest to the Chemical Pulping and Bleaching Project Advisory Committee. This is not a dues-funded project in the usual sense; however, member dues contribute to all student activities. The format of this section is that of a paper submitted for publication.

Abstract

Kraft pulp was bleached with chlorine tagged with ^{36}Cl. The octanol:water partition coefficient (K_{ow}) of the collective labeled organic products in the spent solution was 0.03, which is identical to the K_{ow} of water. This unusually low value is believed to arise from a low activity coefficient in water combined with a corresponding high value in octanol. It follows that chlorinated bleach mill effluents will tend to move with the water column. Biological effects are likely to be associated with the small proportion of lipophilic components in the effluent which should progressively partition out of the water column with flow. Hence, a direct correlation between total organochlorine concentration and biological effect is not expected. Chlorinated materials formed in the pulp matrix did not leach significantly into octanol.

LIPOPHILICITY OF A SYNTHETIC BLEACHED KRAFT PULP

Introduction

An average of 5 kg. of chlorinated organic material results from each metric ton of Kraft pulp bleached by conventional chlorine-based sequences (1,2). Bleached Kraft mill effluent (BKME) contains high-profile contaminants such as chlorophenols as well as numerous high molecular weight compounds that are largely uncharacterized (1,3). Although the lipophilicity of many BKME components is known (4), a composite K_{ow} value that applies to all the chlorinated compounds in BKME is not available. In this study, we determine this K_{ow} in order to model the environmental transport and distribution of the chlorinated component of BKME.

Experimental

An oxygen-delignified and a non-oxygen delignified Southern pine Kraft pulp of kappa number 14.7 and 26.6, respectively, were used. The pulps were hand-washed and brought to 24% consistency (solids level in water) by vacuum filtration with recycling of filtrate. Radioactive chloride ($^{36}Cl^-$) as HCl (9.48 mCi/g) was purchased from du Pont.

Scintillation counting was done on a Beckman 3704 instrument. A counting efficiency of 88% was determined for ^{36}Cl.

Preparation of Radioactive Chlorine

Molecular chlorine is in equilibrium with ionic species through the processes

$$Cl_2 + H_2O = HOCl + HCl$$
$$Cl_2 + Cl^- = Cl_3^-$$

Thus, if $^{36}Cl^-$ is added to an aqueous chlorine solution, the isotope should rapidly equilibrate to give labeled chlorine. In order to verify this, a chlorine solution containing $^{36}Cl^-$ was added to an aqueous solution of phenol at pH 11. The chlorination of phenol is rapid and forms mostly chlorophenol when the phenol is held in excess. If radioactive chlorine is formed as expected, then approximately half the isotope should be converted to chlorophenol.

The solution was acidified with concentrated nitric acid after a 30 minute reaction period, extracted with toluene, and counted for radioactivity. If all the chlorinated products from phenol extracted into toluene, then half of the initial radioactivity would transfer to the toluene phase with the other half remaining in water as inorganic chloride. We found the organic:aqueous phase distribution of radioactivity to be 40:60. Clearly, the added $^{36}Cl^-$ is cycled into labeled molecular chlorine.

Pulp:water Distribution of Chloride Ion

One of our objectives was to determine the fraction of the initial chlorine applied that terminates in products inextricably bound to pulp. In order to assign all the counts in pulp to organochlorine products, it was necessary to verify that chloride ion has a very low affinity for pulp. A Kraft loblolly pine pulp suspension at 3% consistency (solids level) was spiked with $^{36}Cl^-$, and the mixture was equilibrated for 1 hour at 60°C. The mixture was then centrifuged, and 97.0±0.1% of the activity was recovered in the solution phase,

confirming the preference of $^{36}Cl^-$ for the aqueous phase.

Bleaching Experiments

Bleaching was conducted in a 40 mL glass vessel sealed with a paraffin-coated stopper. Pulp (0.5 g. on an oven-dried basis at 3% consistency) and the bleaching agent were sequentially added to the vessel, and the mixture was mechanically stirred at 50°C for 1 hour. During Cl_2/ClO_2 bleaching, the ClO_2 was added 1 minute prior to Cl_2 addition. The mixture was vacuum-filtered, and the solids resuspended to 5% consistency for the caustic extraction stage. NaOH was added to the pulp suspension and the mixture stirred for 1 hour at 70°C. The suspension was again vacuum-filtered, and the pulp washed with water.

The chlorination/extraction conditions were as follows.

(a) 100% Cl_2; 3.4% active chlorine applied; extraction stage: 40% and 7% NaOH by weight;

(b) 76% Cl_2 and 23% ClO_2; 3.9% active chlorine applied; extraction stage: 40% and 7% NaOH by weight;

(c) 100% Cl_2; 4.3% active chlorine applied; extraction stage: 7% NaOH by weight.

The percent active chlorine applied is the weight of the Cl_2 and ClO_2 (in Cl_2 equivalents) applied per 100 g. of oven-dried pulp.

The component of the filtrate associated with chlorinated organics was determined from the counts as follows. In a typical experiment, the filtrate contained 17,341 dpm/mL. The activity in the initial ^{36}Cl stock solution (before its addition to aqueous chlorine) was 2.164E10 dpm/g. Thus, the activity in the filtrate corresponds to 0.801 ppm of ^{36}Cl material. The Cl_2 mass in the bleaching solution was 17.17 mg. as determined by iodometric titration. A count of the solution showed its ^{36}Cl content to be 0.0163 mg. Thus, ^{36}Cl constituted 0.095% of the total chlorine mass.

Chloride ion was determined to be 395 ppm in the filtrate by ion chromatography.

Of this, 0.095% or 0.374 ppm was $^{36}Cl^-$. Since the filtrate contained 0.801 ppm of ^{36}Cl as discussed above, the difference (0.427 ppm) of ^{36}Cl must be associated with tagged chlorinated organic products. Thus, the chlorine fraction of the total labeled and unlabeled chlorinated organic products (Cl_{org}) is 0.427/0.00095 or 450 ppm.

Pulp was separated from the mixture by vacuum filtration. The filtrate was recycled through the pulp mat in order to simulate actual mill operating conditions and to recapture fines. The extracted pulp was washed with 5 mL of 70°C distilled water prior to collection and storage.

Octanol Extractions

The filtrates were extracted with an equal volume (2 mL: 2 mL) of octanol. Pulp (0.5 g.) at 32% consistency was extracted with 2 mL of octanol. Octanol extractions were done by shaking vigorously for 10 minutes and allowing the phases to separate over 48 hours. The octanol:water partitioning of chloride ion was expected to be very small, and to confirm this, $^{36}Cl^-$ (1420 dpm) as HCl was added to 1 mL of water and extracted with 1 mL of octanol. No counts were detected in the octanol phase. This result is consistent with the reported value of 0.001 (5) for the K_{ow} of NaCl.

The tagged material in the filtrate represents both chloride ion and chlorinated organic material. In order to obtain the octanol:water distribution coefficient (K_{ow}) of the chlorinated organic compounds, the activity in the octanol and water phases was measured by scintillation counting. The activity in the octanol phase was attributed in its entirety to chlorinated organics. That in the water phase was corrected for $^{36}Cl^-$ activity determined through ion chromatography.

Results and Discussion

The distribution of effluent components was determined with radiolabeled material prepared by bleaching pulp with $^{36}Cl_2$. Use of ^{36}Cl allows the direct and unambiguous quantitation of organochlorine in water, octanol, and pulp. The activity in the filtrates

and pulps determined at various stages of the bleaching sequence is presented in Table 1. Recoveries range between 69% and 82%, and the loss probably reflects the escape of chlorine gas and volatile products. As expected, the bulk (80%-84%) of the recovered activity was found in the C-stage filtrate. No radioactivity was released when the pulp fraction in Table 1 was extracted with octanol, confirming that most of the chlorinated material in pulp is inextricably bound and is presumably not bioavailable.

The C-stage pulp used in the first entry of Table 1 was extracted as a function of NaOH concentration, and the activity recovered is listed in Table 2. No real improvement in extraction efficiency occurs beyond a charge of 7% NaOH. It would seem that the lower levels of caustic remove Cl^- and low molecular weight materials, and the larger compounds dissolve at higher caustic strength.

The Table 1 data suggest that most of the activity remaining in the pulp after the C-stage can be removed in the E-stage. The C-stage data in Table 1 are further expanded into Cl^- and Cl_{org} fractions in Table 3. No real differences in the $[Cl^-]$:$[Cl_{org}]$ ratio can be interpreted owing to the high uncertainty. This value is a measure of the ratio of oxidation to substitution between lignin and the oxidant. The K_{ow} values in Table 3 are similar for all the conditions examined, and average out to 0.03. This remarkably low value is the same as that for water (6). Although organic compounds that are as lipophobic as water are relatively uncommon, there is ample available precedent (7). For example, the K_{ow} for sucrose is $K_{ow}=0.0002$; that for glycerol is 0.02. Activity coefficients for highly polar compounds in the octanol phase (γ_{oct}) are much higher than those for the water phase (γ_w). Also, activity coefficients in octanol tend to increase with molecular size (6,8,9). It has recently been shown (10) that the molecular weight of chlorinated material in BKME averages to 200-550. Highly polar materials in this weight fraction should give rise to a low γ_w and a high γ_{oct}, which translates to a low K_{ow} value.

It is known that about 0.1% of BKME components have $K_{ow}>3$ (3). These are the

compounds of principal environmental concern, and their mobility will be attenuated by sorption to soil and sediment. Thus, the environmentally important components will be less mobile than the others, and a correlation between environmental effects and total chlorine load is not expected. These conclusions are consistent with the work of Hodson et al. (11) who demonstrated differential mobility for a number of effluent components. The majority of the components, however, will tend to move with the water column; their low K_{ow} provides a basis for recent observations (11,12) of their presence 100 km. downstream of the mill.

In summary, the average lipophilicity of BKME is about the same as that of water, and the transport of these materials should parallel that of water. The bioconcentration potential of these compounds are minimal, and their primary removal mechanism from the water column should be through degradation. It is strongly emphasized that these conclusions apply to BKME as a family, and should not be applied to a subset of components contained therein.

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Acknowledgment

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Table 1: Distribution of ^{36}Cl in Pulp and Effluents

pulp type[b]	percent Cl applied	percent NaOH applied	recovery[c]	percent distribution of recovered ^{36}Cl[a] C	E	E_{pw}	pulp
A	3.4	40	82	80	13	2	5
		7	82	83	14	1	3
A	3.9[d]	40	77	82	15	1	1
		7	69	83	13	2	3
A	4.3	7	79	82	13	2	3
B	3.4	7	82	85	13	1	1

[a]C:chlorination effluent; E:extraction effluent; E_{pw}: pulp wash following extraction; [b]A: oxygen delignified; B: non-oxygen delignified; [c]of total ^{36}Cl applied; [d]23% ClO_2 substitution.

Table 2: E stage extraction efficiency vs. applied alkali

percent caustic applied	percent activity recovered
0	5
1	6
2	7
4	8
7	14
40	15

Table 3: K_{ow} values for C-Stage Effluent

pulp type[a]	percent Cl applied	$[Cl^-]$ ppm	$[Cl_{org}]$ ppm	K_{ow}	n
A	3.4	468±48	363±58	0.027±0.08	3
A	3.9[b]	393±15	278±126	0.046±0.026	3
A	4.3	692±170	264±60	0.029±0.013	3
B	3.4	977	385	0.029	1

[a] A: oxygen delignified; B: non-oxygen delignified;
[b] 23% ClO_2 substitution.